THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Appellant:	§	
	§	Group Art Unit: 1714
CHARLES A. LIEDER	§	
LLOYD E. FUNK	§	Examiner: C. Toomer
DAVID A. BARKER	§	
	§	
Filed: April 21, 2000	§	
	§	
Serial No.: 09/556,852	§	
	§	
For: GASOLINE-OXYGENATE BLEND	§	
AND METHOD OF PRODUCING	§	
THE SAME	§	Attorney Docket No.: 013129-00025

APPEAL BRIEF

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<u>AMENDED APPEAL BRIEF</u>

MAIL STOP APPEAL BRIEF - PATENTS
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In response to a Notification of Non-Compliant Appeal Brief mailed January 30, 2006, and having a period of reply of 30 days, Appellants hereby submit this Amended Appeal Brief, in single copy as per MPEP 1205.02 [R-3]. This Amended Appeal Brief is believed to be timely filed and in compliance with 37 C.F.R. § 41.37. No additional fees are believed to be due in association with this submission. However, should any fees under 37 C.F.R. §§ 1.16 to 1.21 or 41.20(b)(2) be required for any reason relating to this document, the Commissioner is authorized to deduct the fees from Locke Liddell & Sapp LLP Deposit Account No. 12-1322 (Ref. No.: 013129-00025).

I.   REAL PARTY IN INTEREST

The real party in interest in this appeal is Shell Oil Company, a corporation formed under the laws of the State of Delaware, to whom this application has been assigned.

II.   RELATED APPEALS AND INTERFERENCES

No related appeals or interferences exist.

III.   STATUS OF CLAIMS

As originally filed, this application contained Claims 1-29. Claims 1-40 are active in this application. The Examiner has rejected Claims 1-40 on the grounds discussed herein. Accordingly, the claims on appeal are Claims 1-40. A copy of the claims on appeal is set forth in the *Appendix*. Each of these claims stands finally rejected for which Appellants bring the present appeal to the Board.

IV.   STATUS OF AMENDMENT

Claims 1, 10, 16-18 23, and 26 were amended in the Amendment and Response to the Office Action Dated September 10, 2004. No amendments were made subsequent to the Final Rejection dated March 3, 2005. All amendments were made prior to the final rejection and have been entered into the record and considered by the Examiner.

V.   SUMMARY OF CLAIMED SUBJECT MATTER
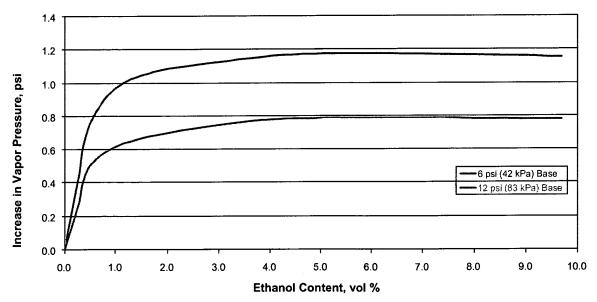
Appellants' invention relates to novel gasoline-oxygenate blends suitable for use in automotive engines containing at least one alcohol. The relatively low boiling point of alcohols (e.g., the boiling point of ethanol is 78 °C), while being significantly higher than the initial boiling point of gasoline (approximately 30 °C), is lower than the mid-boiling point of gasoline

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(approximately 100°C). The vapor pressure of neat alcohols is lower than that of gasoline. Consequently one would expect that blending an alcohol with gasoline would reduce the Reid Vapor Pressure ("RVP") (defined in ll. 5-8, p. 7) and somewhat increase mid-range volatility. However, when alcohol is blended with gasoline at concentrations up to around 30%, there is an unexpected increase in vapor pressure which causes the blend to have significantly higher RVP than the base gasoline. This is shown in FIG. 1 below for ethanol:

FIG. 1

Effect of ethanol addition on Reid Vapor Pressure (RPV) at two levels of base fuel RVP

The effect of alcohols, such as methanol and ethanol, on the increase in vapor pressure of a gasoline blend is further reported in Chapter 2 of API Publication 4261, a copy of which was attached to the Amendment and Response to Office Action of June 4, 2002, filed on October 4, 2002. Note in particular Figs. 9, 10 and 11. As clearly shown in Figure 9, the maximum RVP increase occurs at around 5-15 % v/v alcohol. This is the level of alcohol in most commercial blends. The resulting blend is often too volatile, unless base fuel volatility is adjusted to meet

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fuel specifications. Fig. 10 of API Publication 4261 further shows that the addition of 10 % v/v ethanol to a base fuel composition typically raises the RVP by about 1 PSI; the increase for 10% v/v methanol being almost 3 PSI.

Gasoline-oxygenate blends of gasoline formulations exhibiting the RVP and alcohol volume specifications recited in the claims of Appellants dramatically reduce (and in most instances, eliminate) the need for methyl t-butyl ether (MTBE) in gasoline formulations. In addition, the claimed gasoline-oxygenate blends provide increased percentile reductions of NOx, toxic pollutants and VOCs. Compare, for instance, the data for Percent Reduction ("% Red") in NO$_x$R, ToxR and VOCR in Table 9 for A2, C2, D2, E2, F2, I2, J2, L2, O2, Q2, R2 and S2 (outside of the claimed blends) versus A1, C1, D1, E1, F1, I1, J1, L1, O1, Q1, R1 and S1, respectively (within the claims of Appellants).

The novel compositions of Appellants meet RVP specifications *by adjustment to the base fuel composition*. Note, for instance, reference to the preferred butane percentile in the FFB (defined in ll. 26-27, p. 14 through l. 2, p. 15 of the specification). This, in turn, causes a reduction in the vapor pressure of the light components of the base gasoline. The addition of alcohol to the base gasoline renders a RVP within the claimed limitations. In one embodiment of the invention, the alcohol may be introduced to the base gasoline at a remote location, such as a distribution terminal. This is often necessary since gasoline containing an alcohol cannot generally be shipped via common pipelines.

VI.   GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The issues on appeal are premised on the grounds of rejection set forth on pages 2-4 of the Final Office Action dated March 8, 2005. The issues are as follows:

1.   Whether Claims 1-9, 17-22, 26-40 fail to comply with the written description requirement under 35 U.S.C. § 112, First Paragraph.

2   Whether Claims 1, 4-10, 13-17, and 23-29 are unpatentable under 35 U.S.C. § 102(b) over U.S. Patent No. 5,679,117 ("*Jarvis*").

GROUPING OF THE CLAIMS

1.   For purposes of the obviousness rejection under 35 U.S.C. § 112, First Paragraph, all the Claims 1-9, 17-22, 26-40 stand or fall together.

2.   For purposes of the anticipation rejection under 35 U.S.C. § 102(b) over *Jarvis*:

(a.)   Claims 1, 4, 7-10, 13, 15-17, and 23-29 stand or fall together; and

(b.)   Claims 5-6 and 14 stand or fall together.

VII.   ARGUMENT

A.   The Examiner Has Improperly Maintained the Rejection of Claims 1-9, 17-22, 26-40 under 35 U.S.C. § 112, First Paragraph.

The Examiner has maintained a rejection of Claims 1, 17, 18, 26, 30, 34, and 38 under 35 U.S.C. § 112, First Paragraph as failing to comply with the written description requirement. The following presents each of the contentions of the Examiner and the written support from the Application as filed for the Claims. In order to comply with the written description requirement, the specification "need not describe the claimed subject matter in exactly the same terms as used in the claims; it must simply indicate to persons skilled in the art that as of the [filing] date the applicant had invented what is now claimed." *E.g.*, *Eiselstein v. Frank*, 52 F.3d 1035, 1038, 34 U.S.P.Q.2d 1467, 1470 (Fed. Cir. 1995) (citing *Vas-Cath Inc. v. Mahurkar*, 935 F.2d 1555, 1562, 19 U.S.P.Q.2d 1111, 1115 (Fed. Cir. 1991) and *In re Wertheim*, 541 F.2d 257, 265, 191 U.S.P.Q. 90, 98 (C.C.P.A. 1976)). "The test for determining compliance with the written description

requirement is whether the disclosure of the application as originally filed reasonably conveys to the artisan that the inventor had possession at that time of the later claimed subject matter, rather than the presence or absence of literal support in the specification for the claim language." *In re Kaslow*, 707 F.2d 1366, 1375, 217 U.S.P.Q. 1089, 1096 (Fed. Cir. 1983). As illustrated below, the Application as filed supported the current Claims.

1. Rejection of Claims 1, 17, and 26.

The Examiner rejected Claims 1, 17, and 26 for the inclusion of "less than or equal to 10 volume percent." Appellants respectfully note that the Specification as filed contained Table 8: Phase I Gasoline-Oxygenate Blend Recipes, that is reprinted herein, which provided support for this element:

TABLE 8: PHASE I GASOLINE-OXYGENATE BLEND RECIPES

BLEND	EtOH	C4	FFB	RAFF	HOR	TOL	LCC	ALKY	LSCC	HCC
	(in terms of volume percent of the total blend) (%)									
A1	9.50	0.00	1.27	0.00	20.72	17.92	8.05	42.54	0.00	0.00
A2	5.42	0.0	1.3	0.0	21.7	18.7	8.4	44.5	0.0	0.0
B2	9.50	0.00	0.00	15.39	16.20	9.41	0.00	23.89	10.59	15.02
B2	5.42	0.0	0.0	16.1	16.9	9.8	0.0	25.0	11.1	15.7
C1	9.50	1.45	0.00	0.00	14.93	27.60	13.39	33.12	0.00	0.00
C2	5.42	1.5	0.0	0.0	15.6	28.8	14.0	34.6	0.0	0.0
D1	9.50	0	0	15.7	24.8	0	12.8	15.7	18.6	2.9
D2	5.42	0.0	0.0	16.5	25.9	0.0	13.3	16.5	19.4	3.0
E1	9.50	0.00	0.00	22.63	25.25	0.00	0.00	15.84	16.83	9.86
E2	5.42	0.0	0.0	23.6	26.4	0.0	0.0	16.6	17.6	10.3
F1	9.50	0.00	0.00	9.14	9.23	32.85	16.47	22.81	0.00	0.00
F2	5.42	0.0	0.0	9.6	9.6	34.3	17.2	23.8	0.0	0.0
G1	9.50	0.09	3.35	0.00	34.39	7.15	9.50	35.93	0.00	0.00
G2	5.42	0.1	3.5	0.0	35.9	7.5	9.9	37.5	0.0	0.0
H	9.50	0.00	0.00	12.49	15.48	0.00	0.09	25.61	18.55	18.19
I1	9.50	0.00	1.81	19.10	8.78	19.28	11.31	9.68	20.54	0.00
I2	5.42	0.0	1.9	20.0	9.2	20.1	11.8	10.1	21.5	0.0
J1	9.50	0.00	1.45	0.00	31.77	9.59	12.94	32.67	0.00	2.08
J2	5.42	0.0	1.5	0.0	33.2	10.0	13.5	34.1	0.0	2.2
K1	9.50	0.00	0.00	20.27	17.47	13.39	7.24	20.72	10.05	1.36
K2	5.42	0.0	0.0	21.2	18.3	14.0	7.6	21.7	10.5	1.4
L1	9.40	0.00	0.00	23.47	16.13	7.34	13.32	10.87	17.03	2.54

BLEND	EtOH	C4	FFB	RAFF	HOR	TOL	LCC	ALKY	LSCC	HCC
	(in terms of volume percent of the total blend) (%)									
L2	5.42	0.0	0.0	24.5	16.8	7.7	13.9	11.3	17.8	2.6
M	9.50	0.00	0.00	11.67	19.10	0.18	9.96	20.27	17.20	12.13
N	9.72	0.00	0.72	18.33	4.15	23.20	17.42	0.00	17.33	9.21
O1	9.79	0.00	2.71	0.00	20.57	15.97	9.11	36.26	0.00	5.68
O2	5.42	0.0	2.8	0.0	21.6	16.7	9.6	38.0	0.0	6.0
P	9.72	0.00	0.00	15.98	0.00	19.23	6.68	19.41	15.80	13.27
Q1	9.64	0.00	0.00	17.80	4.70	14.64	3.34	12.83	18.61	18.52
Q2	5.42	0.0	0.0	18.6	4.9	15.3	3.5	13.4	19.5	19.4
R1	9.59	0.00	0.00	20.52	17.36	5.33	7.23	5.79	23.87	10.22
R2	5.42	0.0	0.0	21.5	18.2	5.6	7.6	6.1	25.0	10.7
S1	9.69	0.00	0.99	11.56	0.00	26.55	14.54	36.76	0.00	0.00
S2	5.42	0.0	1.0	12.1	0.0	27.8	15.2	38.5	0.0	0.0
T	9.66	0	0	13.5	15.3	4.2	15.4	12.3	26.6	3.3
U	9.66	0	0	4.2	12.8	15.7	7.5	32.2	0	17.9
V	9.81	0	0	19.1	13.3	0	0	17.2	26.8	13.7
W	9.67	0	0	0	32	11.8	26.7	19.7	0	0
X	9.65	0	0	9.7	0	0.4	0.73	34.5	24	21.1

Application, pp. 20-21. These blends show "an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent" as labeled EtOH column in this example. As shown, the EtOH or alcohol content of samples A1-X contain an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.

Similarly, Appellants respectfully note that the Specification as filed contained Table 13: Phase II Gasoline-Oxygenate Blend Recipes, that is reprinted herein:

TABLE 13: PHASE II GASOLINE-OXYGENATE BLEND RECIPES

BLEND	EtOH	C4	FFB	RAFF	HOR	TOL	LCC	ALKY	LSCC	HCC
	(in terms of volume percent of the total blend) (%)									
AA	9.750	0.0	4.1	13.3	14.0	24.0	0.0	34.9	0.0	0.0
BB	9.900	0.0	0.0	18.2	17.6	0.0	18.7	13.7	19.7	2.3
CC	9.680	0.0	0.0	16.4	30.3	0.2	0.0	24.6	1.4	17.3
DD1	9.610	0.0	1.5	0.1	11.6	16.5	19.6	35.2	6.1	0.0
DD2	5.420	0.0	1.6	0.1	12.1	17.2	20.5	36.8	6.3	0.0
EE1	9.450	0.0	0.2	2.2	2.1	24.8	22.9	36.6	1.8	0.0
EE2	5.420	0.0	0.2	2.3	2.2	25.9	23.9	38.2	1.9	0.0
FF	9.640	0.4	0.0	20.6	30.5	0.0	1.5	16.0	8.0	13.4
GG	9.560	0.0	4.4	6.4	15.7	35.2	16.4	12.3	0.0	0.0
HH	9.910	0.8	0.2	21.2	36.7	0.2	4.1	4.8	13.2	8.9
II	9.760	0.0	2.0	2.9	34.9	12.4	15.2	21.7	0.0	1.3
JJ	9.660	0.0	0.0	25.2	0.1	18.6	15.0	12.3	19.2	0.0
KK1	9.620	0.0	0.6	5.3	4.2	28.6	20.2	31.6	0.0	0.0
KK2	5.420	0.0	0.7	5.6	4.4	29.9	21.1	33.1	0.0	0.0

Application, p. 27. These blends show "an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent" as labeled EtOH column in this example. As shown, the EtOH or alcohol content of samples AA-KK2 contain an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.

Accordingly, there is support for the limitation of this range in Claims 1, 17, 26, and their dependencies. The tables include sufficient data regarding the alcohol content to show that the Appellants were in possession of the invention.

2.   Rejection of Claim 18.

With respect to the requirement of a "benzene content of the blend is greater than 0.27 volume percent" in Claim 18 and its dependencies, the Appellants note that in Table 10: Additional Phase I Gasoline-Oxygenate Blend Properties, Blend X contains a 0.27 Volume Percent Benzene. The Table from the specification is reprinted below:

TABLE 10: ADDITIONAL PHASE I GASOLINE-OXYGENATE BLEND PROPERTIES

Blend	Oxy Wt%	Benz Vol%	Sulfur PPMW	Olef Vol%	Arom Vol%	NOxR % Red	ToxR % Red	VOCR % Red
A1	3.54	0.53	23	1.41	23.25	15.7	40.4	47.5
A2	2.02	0.55	24	1.47	24.30	15.8	39.5	43.9
B1	3.49	0.58	197	2.90	25.01	7.2	34.5	39.5
B2	1.99	0.61	206	3.03	26.14	7.1	33.1	35.9
C1	3.47	0.53	34	2.31	33.89	13.5	35.2	44.6
C2	1.98	0.55	36	2.41	35.41	13.1	32.7	37.8
D1	3.56	0.71	80	3.68	23.75	12.1	33.4	33.8
D2	2.03	0.75	84	3.85	24.83	12.0	32.8	31.1
E1	3.58	0.68	143	1.92	24.34	9.3	33.2	37.4
E2	2.04	0.71	149	2.01	25.43	9.4	32.6	37.2
F1	3.48	0.63	70	4.61	32.97	11.4	34.3	45.6
F2	1.99	0.66	73	4.82	34.46	11.7	32.3	45.6
G1	3.46	0.67	36	2.10	25.73	14.1	36	39.8
G2	1.97	0.70	38	2.20	26.89	14.4	35.4	41.3
H	3.55	0.52	261	4.30	16.76	7.5	36.8	39.3
I1	3.52	0.70	68	3.08	31.08	11.5	32.1	37.8
I2	2.01	0.73	71	3.21	32.48	11.6	30.9	36.1
J1	3.53	0.85	83	3.79	28.20	11.5	31.8	41.7
J2	2.01	0.89	87	3.96	29.47	11.6	29.9	39.0
K1	3.54	1.05	106	2.38	24.83	10.5	29.9	36.6
K2	2.02	1.10	111	2.49	25.95	10.6	29.3	40.4
L1	3.45	0.69	108	2.82	27.83	9.9	33.6	39.9
L2	1.99	0.72	113	2.94	29.06	9.7	32.7	38.2
M	3.50	0.77	215	4.70	26.14	6	30.3	37.6
N	3.51	0.78	247	7.39	31.62	3.2	27.1	35.6
O1	3.59	0.64	116	3.99	28.50	9.9	33.8	37.5
O2	1.99	0.67	122	4.18	29.88	9.8	32.4	36.4
P	3.56	0.51	213	3.06	25.15	6.2	35.8	38.3
Q1	3.50	0.69	260	1.15	30.83	3.9	28.2	36.7
Q2	1.97	0.73	272	1.21	32.27	3.7	26.3	33.6
R1	3.54	0.85	177	4.55	27.11	7.1	28.8	33.3
R2	2.00	0.89	185	4.76	28.36	7.1	27.5	32.6
S1	3.59	0.56	88	4.20	23.60	11.8	39.1	38.7
S2	2.01	0.59	92	4.40	24.71	11.8	37.7	36.5
T	3.54	0.73	128	2.11	28.15	9.3	31.4	38.3
U	3.54	0.49	250	4.86	25.18	5.3	35.3	39.2
V	3.61	0.64	177	3.32	22.57	8.4	34.1	37.4
W	3.50	0.81	110	5.41	33.39	9.1	29.9	38.3

Blend	Oxy Wt%	Benz Vol%	Sulfur PPMW	Olef Vol%	Arom Vol%	NOxR % Red	ToxR % Red	VOCR % Red
X	3.58	0.27	286	5.92	32.65	2.7	32.4	35.2

Application, pp. 24-25. Accordingly, there is support for the limitation of this range in Claim 18 and its dependencies. The table includes sufficient data to show that the Appellants were in possession of the invention and provided a written description of same; accordingly a reconsideration is respectfully requested.

3. Rejection of Claim 30.

With respect to the requirement of a "the aromatic content of the blend is greater than 16.76 volume percent" in Claim 30 and its dependencies, Appellants note that in Table 10: Additional Phase I Gasoline-Oxygenate Blend Properties, Blend H contains an aromatic content of the blend of 16.76 volume percent is disclosed. The Table was reprinted above.

Accordingly, there is support for the limitation of this range in Claim 30 and its dependencies. The table includes sufficient data to show that the Appellants were in possession of the invention and provided an adequate description.

4. Rejection of Claim 34.

With respect to the requirement of "the olefin content of the blend is greater than 1.15 volume percent" in Claim 34 and its dependencies, the Appellants note that in Table 10: Additional Phase I Gasoline-Oxygenate Blend Properties, Blend Q1 contains an olefin content of 1.15 volume percent. The Table was reprinted above.

Accordingly, there is support for the limitation of this range in Claim 34 and its dependencies. The table includes sufficient data to show that the Appellants were in possession of the invention.

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5.   Rejection of Claim 38.

With respect to the requirement of "a Dry Vapor Pressure Equivalent greater than or equal to 5.3 PSI" in Claim 38 and its dependencies, the Appellants note that in Table 12: Phase Ii Neat Blend Recipes Properties, Blends BB and CC contain a Dry Vapor Pressure Equivalent of 5.3 PSI. This limitation is also disclosed. The Table is reprinted below.

TABLE 12: PHASE II NEAT BLEND RECIPES PROPERTIES

Blend	RON	MON	(R+M)/2	DVPE	T10	T50	T90	EP	E200	E300
				PSI	°F	°F	°F	°F	Vol. %	Vol. %
AA	96.5	87.5	92.0	5.5	156.3	224.5	308.5	387.0	30.5	88.0
BB	88.1	81.9	85.0	5.3	145.4	213.7	342.0	415.5	42.9	79.1
CC	90.7	83.6	87.2	5.3	150.6	214.7	327.7	406.2	40.0	83.1
DD	96.3	87.7	92.0	5.5	151.4	222.6	308.3	398.3	33.1	88.1
EE	96.6	87.9	92.3	5.5	159.0	217.1	277.0	375.7	33.9	92.1
FF	89.8	82.5	86.2	5.5	145.9	218.4	336.0	414.6	40.2	79.9
GG	97.2	86.8	92.0	5.5	153.8	228.1	303.9	386.3	29.9	88.8
HH	89.0	81.8	85.4	5.5	146.3	231.5	340.8	416.3	36.9	75.1
II	96.4	87.2	91.8	5.5	152.7	231.4	323.4	393.0	30.3	83.2
JJ	88.4	81.9	85.2	5.4	150.1	213.0	322.6	414.5	41.1	85.4
KK	96.6	87.0	91.8	5.4	159.9	218.4	281.2	374.0	32.8	92.1

Application, p. 26.

Accordingly, support for the limitation of this range in Claim 38 and its dependencies is present in the specification. The table includes sufficient data to show that the Appellants were in possession of the invention and disclosed same. The written description requirement is supported by the data provided in the Specification as filed. Accordingly, the grounds of rejection over the written requirement should be reversed.

B.   The Examiner Has Improperly Maintained the Rejection of Claims 1, 4-10, 13-17 and 23-29 Under 35 U.S.C. §102(b) Over *Jarvis*.

The Examiner has rejected Claims 1, 4-10, 13-17, and 23-29 under 35 U.S.C. § 102(b) as being anticipated by *Jarvis*. To anticipate a claim, a reference must disclose every limitation of the claimed invention either explicitly or inherently. *In re Schreiber*, 44 U.S.P.Q.2d 1429, 1431 (Fed. Cir. 1997).

1.   Claims 1, 4, 7-10, 13, 15-17, and 23-29 are Not Anticipated by *Jarvis*.

Jarvis does not disclose the alcohol content of the "final product." Though a contestable RVP is listed for this final product, all of the rejected claims also recite an alcohol content. Claim 1 recites "an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent." Claim 26 recites "an alcohol content less than or equal to 10 volume percent." Claims 10 and 23 recite "an alcohol content greater than about 5.0 volume percent." *Jarvis* fails to provide disclosure of an alcohol content of the "final product."

Moreover, *Jarvis* fails to disclose a *blend* of gasoline and oxygenate. *Jarvis* discloses a reaction product, not a blend, of gasoline and an oxygenate. Each of Claims 1, 4-10, 13-17, and 23-29 specifically recite a gasoline-oxygenate blend. Appellants provided Declaration of Charles A. Lieder, Ph.D., under 37 C.F.R. § 1.132, submitted with Response to Office Action of February 10, 2003, filed on April 9, 2003, which established that *Jarvis* was directed to a chemical reaction and not a blend. The Examiner has failed to address the conclusions reached by Dr. Lieder that *Jarvis* is drawn to a reaction product because *Jarvis*:

(1)   discloses the use of a platinum catalyst in "an elongated catalyzing chamber" (lines 25-27 of column 1 of *Jarvis*). Catalysts are used to accelerate chemical reactions and are not useful in blends of mixtures;

(2)   characterizes his product as being derived from a "catalyzed mixture";

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(3)   demonstrates a disparity in the reported physical properties of the products and the theoretical physical properties of the products (discussed below); and

(4)   recites conditions characteristic of chemical reactions, as set forth in 1. 25, col. 4 through 1. 3., col. 5. *See* further paragraph 6 of Declaration of Dr. Lieder.

Because *Jarvis* fails to disclose a *blend* of gasoline and oxygenate and because each of Claims 1, 4-10, 13-17, and 23-29 recite an alcohol content that is not disclosed by the "final product" of *Jarvis*, the grounds of rejection over *Jarvis* should be reversed.

2.   Claims 5-6 and 14 Do Not Stand or Fall With the Other Claims.

Even if independent Claims 1, 18, 23 and 26 and dependent claims 4, 7-9, 13, 15-17, 21-22, 24-25 and 27-29 are anticipated by *Jarvis*, which they are not, Claims 5-6 and 14 are not anticipated by *Jarvis* and must be considered independently because *Jarvis* does not address the need for reducing toxic air pollutants emissions, much less provide a percentile amount for the reduction in toxic air pollutant emissions by the use of the disclosed hydrocarbons. Thus, Claims 5-6 and 14 are not anticipated by *Jarvis*.

Further, the Examiner has not argued that the rejection of Claims 5-6 and 14 is based on inherency and cannot now meet such a burden. *Ex parte Levy*, 17 U.S.P.Q.2d 1461, 1464 (Bd. Pat. App. & Int. 1990) (the Examiner must show "a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art.").

CONCLUSION

The rejections of:

- Claims 1-9, 17-22, 26-40 under 35 U.S.C. § 112, First Paragraph; and

- Claims 1, 4-10, 13-17, and 23-29 under 35 U.S.C. § 102(b) over *Jarvis*

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are improper for the reasons discussed herein. Accordingly, Claims 1-40 are in condition for

allowance and the rejections of the Examiner should be REVERSED.

A decision of the Board consistent with this showing is earnestly requested.

Respectfully submitted,

Date: February 28, 2006

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_____
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VIII. CLAIMS APPENDIX

1.   A gasoline-oxygenate blend, suitable for combustion in an automotive engine, having the following properties:

(a)   a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

(b)   an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.

2.   The blend of Claim 1 wherein the blend has a 50% distillation point less than about 195°F.

3.   The blend of Claim 1 wherein the blend has a 10% distillation point less than about 126°F.

4.   The blend of Claim 1 wherein the blend has an anti-knock index greater than or equal to about 89.

5.   The blend of Claim 1 wherein the blend is capable of reducing toxic air pollutants emissions by more than about 21.5%.

6.   The blend of Claim 5 wherein the blend is capable of reducing toxic air pollutants emissions by more than about 30%.

7.   The blend of Claim 1 wherein the blend has an oxygen weight percent that is greater than about 1.8 weight percent.

8.   The blend of Claim 1 wherein the blend contains ethanol.

9.   The blend of Claim 1 wherein the blend contains essentially no methyl t-butyl ether.

10. A gasoline-oxygenate blend, suitable for combustion in an automotive engine, comprising at least two hydrocarbon streams and an oxygenate stream consisting essentially of an alcohol and having:

a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

an alcohol content greater than about 5.0 volume percent.

11. The blend of Claim 10 wherein the blend has a 50% distillation point less than about 178°F.

12. The blend of Claim 10 wherein the blend has a 10% distillation point less than about 123°F.

13. The blend of Claim 10 wherein the blend has an anti-knock index greater than about 89.

14. The blend of Claim 10 wherein the blend is capable of reducing toxic air pollutants emissions by more than about 21.5%.

15. The blend of Claim 10 wherein the blend has an oxygen weight percent that is greater than about 1.8 weight percent.

16. The blend of Claim 10 wherein the oxygenate stream contains ethanol.

17. The blend of Claim 10 wherein the blend contains less than or equal to 10 volume percent of alcohol.

18. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties:

(a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

(b) an alcohol content greater than about 5.0 volume percent

wherein the benzene content of the blend is greater than 0.27 volume percent.

19. The blend of Claim 18 wherein the blend has a 50% distillation point less than about 250°F.

20. The blend of Claim 18 wherein the blend has a 10% distillation point less than about 158°F.

21. The blend of Claim 18 wherein the blend contains ethanol.

22. The blend of Claim 18 wherein the blend contains essentially no methyl t-butyl ether.

23. A process for preparing a gasoline-oxygenate blend comprising combining a blend of hydrocarbons with a stream consisting essentially of an alcohol, wherein the resulting gasoline-oxygenate blend has the following properties:

  (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

  (b) an alcohol content greater than about 5.0 volume percent.

24. The process of Claim 23 wherein the alcohol is ethanol.

25. The process of Claim 23 wherein the resulting blend contains essentially no methyl t-butyl ether.

26. A process for preparing a gasoline-oxygenate blend comprising combining a blend of hydrocarbons with an alcohol, wherein the resulting gasoline-oxygenate blend has

a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

an alcohol content less than or equal to 10 volume percent.

27. The process of Claim 26 wherein the alcohol is ethanol.

28. The process of Claim 26 further comprising introducing ethanol during the blending.

29. The process of Claim 26 wherein the resulting gasoline-oxygenate blend contains essentially no methyl t-butyl ether.

30. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties:

(a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

(b) an alcohol content greater than about 5.0 volume percent

wherein the aromatic content of the blend is greater than 16.76 volume percent.

31. The blend of Claim 30 wherein the blend has a 50% distillation point less than about 250°F.

32. The blend of Claim 30 wherein the blend has a 10% distillation point less than about 158°F.

33. The blend of Claim 30 wherein the blend contains ethanol.

34. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties:

(a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and

(b) an alcohol content greater than about 5.0 volume percent

wherein the olefin content of the blend is greater than 1.15 volume percent.

35. The blend of Claim 34 wherein the blend has a 50% distillation point less than about 250°F.

36. The blend of Claim 34 wherein the blend has a 10% distillation point less than about 158°F.

37. The blend of Claim 34 wherein the blend contains ethanol.

38. A process for preparing a gasoline-oxygenate blend which comprises adjusting a hydrocarbon base fuel having a Dry Vapor Pressure Equivalent greater than or equal to 5.3 PSI with an alcohol, wherein the Dry Vapor Pressure Equivalent of the gasoline-

oxygenate blend is not greater than 7.2 PSI and further wherein the alcohol content of the gasoline-oxygenate blend is greater than about 5.0 volume percent.

39. The process of Claim 38 wherein the alcohol is ethanol.

40. The process of Claim 38 wherein the resulting gasoline-oxygenate blend contains essentially no methyl t-butyl ether.

IX. EVIDENCE APPENDIX

In compliance with 37 C.F.R. § 41.37, paragraph c(1)(ix), there are enclosed the following copies of evidence previously entered into the record by the Appellants and/or the Examiner, and relied upon herein. These copies of evidence are attached at the end of this Appeal Brief as TABs 1, 2, and 3, wherein:

- TAB 1 is Chapter 2 of API Publication No. 4261, which was originally attached to the Amendment in Response to Office Action of June 4, 2002, filed October 4, 2002, and referenced within the present Appeal Brief on page 4;

- TAB 2 is U.S. Patent No. 5,679,117 to Jarvis, *et al.*, originally disclosed by Appellants in the Supplemental Information Disclosure Statement filed April 3, 2001, cited by the Examiner in the Office Action mailed June 4, 2002, and referenced within the present Appeal Brief on pages 13-14; and

- TAB 3 is the Declaration of Charles A. Lieder, Ph.D. (and the associated Exhibits A and B) under 37 C.F.R. § 1.132, submitted with the Response to Office Action of September 10, 2004, filed on December 13, 2004, and referenced within the present Appeal Brief on pages 13-14.

X. RELATED PRODEEDINGS APPENDIX

None.

Alcohols and Ethers

A Technical Assessment of Their Application as Fuels and Fuel Components

API PUBLICATION 4261
SECOND EDITION, JULY 1988

Alcohols and Ethers

A Technical Assessment of Their Application as Fuels and Fuel Components

Refining Department

API PUBLICATION 4261
SECOND EDITION, JULY 1988

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FOREWORD

This publication was prepared by a task force of the Fuels Subcommittee of the API Products Committee, a joint committee of the API Marketing and Refining Departments. The API Health and Environment Committees and the Industry Affairs Group consisting of Transportation, Safety and Fire Protection, Measurement, and Marketing Operations and Engineering Committees assisted the work. It is based on published information and on private reports from API member companies. The assistance of these companies is gratefully acknowledged. Richard L. Courtney and William P. Dugan served as consultants to the task force.

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CONTENTS

Alcohols and Ethers — A Technical Assessment of Their Application as Fuels and Fuel Components

CHAPTER 1—INTRODUCTION AND SCOPE

In 1971 the American Petroleum Institute (API) studied the feasibility of blending ethanol with gasoline to augment domestic fuel supplies for transportation.[1] After the first Arab oil embargo in 1974 interest in using alcohols as fuels expanded to include methanol, not only as a transportation fuel but also as fuel for stationary power sources. In response to that expanded interest the API published an updated technical assessment in 1976.[2]

Since 1976 many changes have occurred in the use of non-petroleum fuels, both neat and in blends with hydrocarbon components. Today the earlier objective of augmenting domestic energy sources has been joined by two newer objectives: a) to produce high octane gasoline without the use of lead alkyls, and b) to reduce the contribution of motor vehicles and stationary sources to air pollution.

The Clean Air Act Amendments of 1977 and proposals for further legislation and regulation, particularly at the state level, have expanded interest in alcohols and ethers. Many new policy issues have arisen, and more are expected in the future. An important objective of this publication is to provide an updated and expanded technical assessment suitable as a foundation for policy discussion.

The transportation fuels industry has been shaped by four important events since 1976: a) the increased use of alcohols as blending components, b) the appearance of marketplace concerns resulting from the misuse of alcohols as blending components, c) the appearance of federal environmental regulations over the composition of motor fuels, and d) the appearance of ethers as fuel components. In the future a fifth event may be added to these: the regulation of motor fuel composition based on health effects of fuel vapors and combustion products.

This technical assessment, therefore, has been expanded to include ethers as well as alcohols. It also considers flexible-fuel vehicles and vehicles intended for use with neat alcohols, neither of which had been developed in 1976.

This publication summarizes information from the technical literature on producing and applying alcohols and ethers as fuels and fuel components. The alcohols and ethers that are considered include a) methanol, ethanol, isopropyl alcohol (IPA), tertiary butyl alcohol (TBA), methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) as fuel components; b) methanol (both neat and mixed with hydrocarbons) and ethanol as transportation fuels; and c) methanol in stationary power sources. This publication assesses the technical advantages and disadvantages of alcohols and ethers with respect to hydrocarbon fuels. The analysis also addresses the following factors: a) the costs associated with producing alcohols and ethers, b) distribution, storage, and fire protection and safety concerns, and c) health and environmental concerns.

CHAPTER 2—CHEMICAL AND PHYSICAL PROPERTIES OF ALCOHOLS AND ETHERS

General

The chemical and physical properties of alcohols and ethers useful as fuel or fuel components are described in this chapter. A sound understanding of the properties of alcohols and ethers and their effects in blends with hydrocarbons is critical to the use of such materials as motor fuels or fuel components.

The characteristic chemical difference between the components of hydrocarbon fuels and oxygenates, such as alcohols and ethers, is the presence of oxygen in the molecule. The formulae and properties for some oxygenates are listed in Table 1. Additional properties are presented in Appendix B. Oxygenates differ substantially from hydrocarbons in such important fuel parameters as the amount of oxygen required to burn them and in the volumes of combustion products as shown in Table 2. In addition, alcohols and ethers, when burned, generate less heat per gallon than do hydrocarbons. The alcohols also require more heat for vaporization than do hydrocarbon fuels. Combustion performance also includes improved antiknock response, which is presently

Table 1—Some Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Formula	CH_3OH	C_2H_5OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$	$(CH_3)_3COCH_3$	$(CH_3)_2(C_2H_5)COCH_3$	C_4 to C_{12}	C_8 to C_{25}
Molecular weight	32.04	46.07	60.09	74.12	88.15	102.18	100-105	200 (approx.)
Composition, weight %								
Carbon	37.5	52.2	60.0	64.8	68.1	70.5	85-88	84-87
Hydrogen	12.6	13.1	13.4	13.6	13.7	13.8	12-15	13-16
Oxygen	49.9	34.7	26.6	21.6	18.2	15.7	0	0
Specific gravity, 60°F/60°F	0.796	0.794	0.789	0.791	0.744	0.77	0.72-0.78	0.81-0.89
Density, lb/gal @60°F	6.63	6.61	6.57	6.59	6.19	6.41	6.0-6.5	6.7-7.4
Boiling temperature, °F	149	172	180	181	131	187	80-437	370-650
Reid vapor pressure, psi	4.6	2.3	1.8	1.8	7.8	1.5	8-15	<0.2
Octane no. (see note b)								
Research octane no.	—	—	—	—	—	—	88-98	—
Motor octane no.	—	—	—	—	—	—	80-88	—
Cetane no. (see note b)	—	—	—	—	—	—	—	40-55
Water solubility, @70°F								
Fuel in water, volume %	100	100	100	100	4.3	—	Negligible	Negligible
Water in fuel, volume %	100	100	100	100	1.4	0.6	Negligible	Negligible
Viscosity								
Centipoise @68°F	0.59	1.19	2.38	4.2 @78°F	0.35	—	0.37-0.44	2.6-4.1
Centipoise @-4°F	1.15	2.84	9.41	Solid	0.60	—	0.60-0.77	9.7-17.6
Flash point, closed cup, °F	52	55	53	52	-14	—	-45	165
Autoignition temperature, °F	867	793	750	892	815	—	495	600 (approx.)
Flammability limits, volume %								
Lower	7.3	4.3	2.0	2.4	1.6	—	1.4	1.0
Higher	36.0	19.0	12.0	8.0	8.4	—	7.6	6.0
Latent heat of vaporization								
Btu/gal @60°F	3,340	2,378	2,100	1,700	863	—	900 (approx.)	710 (approx.)
Btu/lb @60°F	506	396	320	258	138	—	150 (approx.)	100 (approx.)
Heating value								
Lower (liquid fuel-water vapor) Btu/lb	8,570	11,500	13,300	14,280	15,100	15,690	18,000-19,000	18,000-19,000
Lower (liquid fuel-water vapor) Btu/gal @60°F	56,800	76,000	87,400	94,100	93,500	100,600	109,000-119,000	126,000-130,800
Stoichiometric air/fuel, weight	6.45	9.00	10.3	11.1	11.7	12.1	14.7	14.7
Ratio moles product/moles $O_2 + N_2$	1.21	1.12	1.10	1.10	1.10	1.09	1.08	1.07

Notes:
[a] See Appendix B for all references.
[b] Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with gasolines. Similar problems exist for cetane rating procedures.

Table 2—Combustion of Alcohols, Ethers, and Hydrocarbons In Air

Fuel	Combustion Reaction Equation[a]
Methanol	$CH_3OH + 1.5O_2 + 5.64 N_2 \longrightarrow$ $CO_2 + 2H_2O + 5.64 N_2$
Ethanol	$C_2H_5OH + 3O_2 + 11.3 N_2 \longrightarrow$ $2CO_2 + 3H_2O + 11.3 N_2$
Isopropyl Alcohol	$C_3H_7OH + 4.5O_2 + 16.93 N_2 \longrightarrow$ $3CO_2 + 4H_2O + 16.93 N_2$
tert-Butyl Alcohol	$C_4H_9OH + 6O_2 + 22.6 N_2 \longrightarrow$ $4CO_2 + 5H_2O + 22.6 N_2$
MTBE	$C_5H_{12}O + 7.5O_2 + 28.2 N_2 \longrightarrow$ $5CO_2 + 6H_2O + 28.2 N_2$
TAME	$C_6H_{14}O + 9O_2 + 33.9 N_2 \longrightarrow$ $6CO_2 + 7H_2O + 33.9 N_2$
Gasoline or Diesel Fuel	$C_nH_{2n+2} + [(3n + 1)/2] O_2 + 3.76 [(3n + 1)/2] N_2 \longrightarrow$ $nCO_2 + (n + 1) H_2O + 3.76 [(3n + 1)/2] N_2$

Note:
[a]Based on an air mixture of 79% nitrogen, 21% oxygen.

an objective of the use of oxygenates as substitutes for, or supplements to, gasoline.

As shown in Figure 1, all alcohols contain the same functional group as water—the OH, or hydroxyl, group. Consequently, like water, their molecules have polar characteristics. The molecular polarity is stronger for alcohols with a small hydrocarbon structure or a low carbon number. Methanol is the lowest-order alcohol in a homologous series. Ethanol is next. Alcohols with a large hydrocarbon structure (for example, TBA) have weak polarity. Neither gasoline nor MTBE contains the OH group; consequently, they have little or no significant polarity. While MTBE does contain oxygen, the oxygen is bound into the molecule differently than it is in alcohols. As shown in Figure 1, the oxygen in MTBE is bound into the carbon chain itself rather than being bound at the end of the chain as an OH group.

The physical phenomenon of molecular polarity has important consequences for blends of alcohols in hydrocarbons. Polar molecules have an affinity for other molecules in proportion to the degree of mutual polarity. Thus, at room temperatures, low molecular weight substances like water or methanol would be gases were they not collapsed into liquids by the highly cohesive molecular forces of hydrogen bonding. However, when methanol is dissolved in a non-polar solvent like gasoline, its molecules become physically separated. This physical separation weakens molecular cohesion and the methanol behaves like a gas, resulting in an otherwise anomalous increase in vapor pressure that peaks at quite low methanol concentrations. If water is present as a second phase, a so-called "water bottom," the methanol's affinity for the highly polar water molecules will cause it to separate from the gasoline into the water phase. These effects are much less pronounced for ethanol and are insignificant for higher carbon number alcohols.

Heating Value

One of the most serious disadvantages to the substitution of oxygenates for motor gasoline, either as components or as a complete fuel, is their lower energy content and heating value. For example, the heating value of a gallon of methanol is about half that of a gallon of gasoline. Thus, at equivalent engine efficiency, a methanol-powered vehicle would be able to travel only about half the distance it could cover using the same volume of gasoline. For other oxygenates de-

Water   Methanol   Ethanol   MTBE

A gasoline hydrocarbon
molecule (Isooctane)

Figure 1—Molecular Structures of Water, Methanol, Ethanol, MTBE, and Gasoline

scribed in this publication, the mileage penalty is not as great and may not be considered serious when they are used as blending agents in concentrations approved by the Environmental Protection Agency (EPA).
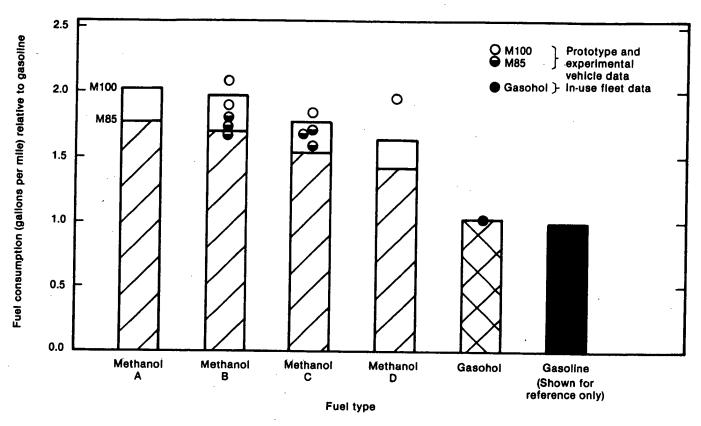
Figure 2 shows the fuel economy that has been obtained when neat methanol and M85, a mixture of 85 percent by volume methanol and 15 percent by volume gasoline, are used instead of gasoline. Because methanol allows improved engine efficiency, as discussed in Chapter 5, vehicle mileage usually is not reduced to the extent predicted by direct calculations based upon heating value differences alone. Furthermore, it has been demonstrated that engines and vehicles can be optimized to take advantage of the vaporization and combustion characteristics of neat methanol to recover additional tank mileage[4-12] (see Figure 2). If it is assumed that M85 allows the same improvements in engine efficiency that are theoretically expected through the use of neat methanol, a fully optimized vehicle would need about 1.5 times more gallons of M85 to travel the same distance as a comparable gasoline vehicle. However, as shown in Figure 2, even the most fuel efficient methanol vehicles presently require at least 1.7 times more M85 and 1.8 times more M100 to travel the same distance as a comparable gasoline vehicle.

Figure 3 shows the same information presented in Figure 2 in terms of energy consumption (Btu/mile). When viewed in this manner, the potential thermodynamic benefits of methanol as a motor fuel appear attractive. Ethanol also offers similar potential for increased engine efficiency; however, as covered in Chapter 3, it is not as economically attractive as methanol as a neat motor fuel.

Energy consumption comparisons from prototype and experimental vehicles are reviewed in Figure 3. Many of the vehicles demonstrated better utilization of potential fuel energy with methanol or M85 than with gasoline. Thermal efficiency improvements approaching 15 percent have been confirmed in some vehicles by means of increased compression ratio and improved combustion. Considerable engine and vehicle development will be required to confirm the theoretical thermal efficiency gains anticipated from lean mixture combustion with methanol.

Octane Performance

Oxygenates can be attractive for use as blending components to increase gasoline octane quality. Adding small percentages of oxygenates to gasoline can produce

Legend:

Methanol A—Relative fuel consumption based on difference in energy content between gasoline and methanol.

Methanol B—Relative fuel consumption assuming a 4 percent thermal efficiency improvement can be achieved due to improved combustion with methanol.

Methanol C—Relative fuel consumption assuming a 15 percent thermal efficiency improvement can be achieved due to improved combustion and increased compression ratio with methanol.

Methanol D—Relative fuel consumption assuming a 25 percent thermal efficiency improvement can be achieved due to improved combustion, increased compression ratio, and optimized lean mixture with methanol.

Source: References 3, 4, 5, 6, 7, 8, and 9.

Figure 2—Vehicle Fuel Consumption (Gallons per Mile) for Oxygenates Expressed Relative to That for Gasoline
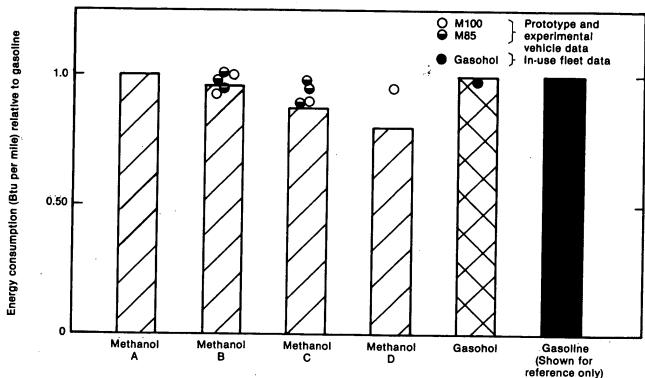
large gains in octane. The incremental value of adding oxygenates to gasoline in terms of the average of Research and Motor octane [(R + M)/2] is shown in Table 3.[13] While methanol has the highest blending octane value, its use without cosolvents is limited by EPA rules governing oxygenate concentrations. Therefore, ethanol and MTBE present the greatest potential octane boost from oxygenates under current rules. The (R + M)/2 increases from oxygenates may not predict Road octane performance as well as similar increases from hydrocarbon blending. Road octane performance (the antiknock performance as measured using passenger cars on the road) of gasoline-oxygenate blends is further discussed in Chapter 4.

As neat fuels for spark-ignition engines many of the oxygenates, particularly those listed in Table 1, provide knock-limited performance superior to that of gasoline. Laboratory engine Research Octane Number (RON) and Motor Octane Number (MON) procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat alcohols and do not represent the octane performance of oxygenates when blended with gasoline. The significance of the potential use of neat oxygenates is dealt with in Chapter 5.

Solubility

Methanol is soluble in hydrocarbons, but the level of solubility depends on hydrocarbon type, temperature, and water content. Methanol is practically insoluble in diesel fuel, and ethanol is only moderately soluble.[14]

Figure 3—Vehicle Energy Consumption (Btu per Mile) for Oxygenates Expressed Relative to That for Gasoline

Legend:

Methanol A—Relative energy consumption based on difference in energy content between gasoline and methanol.

Methanol B—Relative energy consumption assuming a 4 percent thermal efficiency improvement can be achieved due to improved combustion with methanol.

Methanol C—Relative energy consumption assuming a 15 percent thermal efficiency improvement can be achieved due to improved combustion and increased compression ratio with methanol.

Methanol D—Relative energy consumption assuming a 25 percent thermal efficiency improvement can be achieved due to improved combustion, increased compression ratio, and optimized lean mixture with methanol.

Source: References 3, 4, 5, 6, 7, 8, and 9.

Table 3—Octane Boost for Selected Oxygenates

Oxygenate	Concentration Limit (Volume Percent)	Basis for Limit	Typical Blending Value[b] (R + M)/2	Boost at Concentration Limit[b]
Ethanol	10.0	Gasohol Waiver (1979)	113	2.6
Methanol	0.3	Substantially Similar (1981)	116	0.1
Methanol/GTBA (1:1 ratio)	9.4[c]	ARCO Waiver 3.5 weight percent oxygen (1981)	107	1.9
MTBE	11.0[c]	Substantially Similar 2.0 weight percent oxygen (1981)	110	2.2

Notes:

[a]Source: Reference 13.

[b]Octane blending values vary with oxygenate concentration, base fuel octane, and composition. Octane boost is calculated for an 87 octane (R + M)/2 unleaded gasoline. See Glossary, Appendix A, Blending Value.

[c]Will vary with base fuel density, since limited by weight percent oxygen.

The solubility of methanol in gasoline is affected by the chemical nature of the hydrocarbons that make up the gasoline. For example, methanol is fully soluble in n-hexane above 100°F, but only about 3 percent will dissolve in n-hexane at 40°F.[15, 16] Methanol and n-octane are only sparingly soluble in each other over the same temperature range.

Methanol dissolves less readily in paraffinic hydrocarbons than it does in aromatic hydrocarbons as shown in Table 4.[17, 18] The variability among gasolines in the ratios of paraffinic to aromatic hydrocarbons, therefore, is a complicating factor in the consideration of blends containing methanol above 5 percent by volume.

Ethanol and higher alcohols dissolve more readily in hydrocarbons than methanol does. They can be used as cosolvents to increase the solubility of methanol in gasoline.[18-24] For example, in a gasoline that dissolved only 3 percent by volume methanol at 32°F, 5 percent by volume isobutyl alcohol increased the methanol solubility to 20 percent by volume, and 5 percent by volume ethanol increased it to 10 percent by volume.

Volume Change of Mixtures of Alcohols and Gasoline
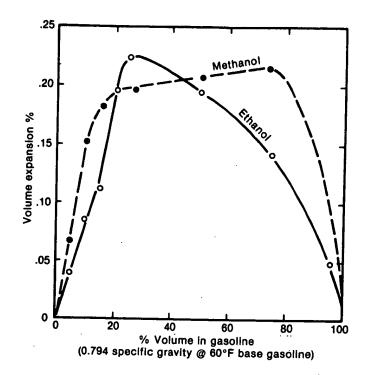
A small but measurable volume expansion effect occurs when alcohols, particularly methanol and ethanol, are added to hydrocarbons. The volume expansion is affected by the density of gasoline. As Figure 4 shows, the

Table 4—Solubility of Methanol in Gasoline

Aromatics in Gasoline, Volume Percent	Methanol Solubility, Volume Percent	
	-10° to 0°F	32° to 37°F
16	2-3	5-10
28	5-10	15-20
31	5-10	> 50
42	> 50	> 50

Gasoline Composition			Minimum Temperature At Which 10% Methanol Will Dissolve, °F
Saturates	Aromatics	Olefins	
100	—	—	80
65	21	14	44
43	2	55	20
20	78	2	4

Source: References 17 and 18.

Source: References 25 and 26.

Figure 4—Volume Increase for Gasoline-Alcohol Blends
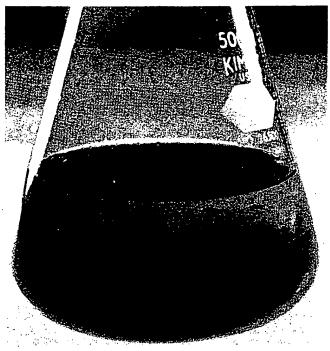
expansion of a gasoline-methanol blend reaches a maximum value of about 0.2 percent over a broad range of concentrations from about 20 to 80 percent methanol. Gasoline-ethanol blends reach about the same maximum expansion but peak sharply at about 20 percent ethanol content.[25, 26] Expansion values for gasoline-ethanol blends as high as 0.55 percent with a 12.5 percent concentration of ethanol have been observed.[27]

Water Sensitivity and Tolerance

The solubility of methanol in gasoline in the presence of water is very limited at room temperature. The solubility of ethanol is better than methanol but is also limited in the presence of water.[25, 26, 28] When small amounts of water are added to a gasoline-methanol blend, hydrogen bonds form between water and methanol molecules and the blend separates into two phases. Paraffinic hydrocarbons predominate in the upper phase, while the lower phase consists primarily of alcohol, water, and small amounts of aromatic hydrocarbons. MTBE has little affinity for water and does not phase separate.

Data on the water sensitivity of gasoline-methanol blends show that blends containing 10 percent by volume methanol must be protected against water in

concentrations greater than 0.05 percent by volume at 70°F,[22] or the blend will separate by the formation of droplets, as shown in Figure 5.[29] A number of higher molecular weight alcohols have been evaluated as cosolvent agents in attempts to increase water tolerance. The use of higher alcohols, including ethanol, as cosolvents to methanol markedly increases the amount of water that can be tolerated at a given temperature.[30] In addition the higher the combined concentration of alcohols, the greater the tolerance for water. Butyl alcohols are very effective cosolvents. Concentrations of 4.5 percent by volume of t-butyl alcohol in combination with 4.5 percent by volume of methanol increase water tolerance above 0.2 percent by volume. Figure 6 shows that water tolerance always increases with temperature.

As shown in Figure 7, the aromatics content of the base gasoline greatly influences the amount of water that can be tolerated without separation.[26] In the range of 14 to 38 percent aromatics content, with cosolvent present, each percent increase in aromatics content reduced the temperature for phase separation by 2–3°F. The benefit of aromatics content, as well as cosolvent

Blend phase separation

Source: Reference 29.

Figure 5—Gasoline-Alcohol Blend Phase Separation
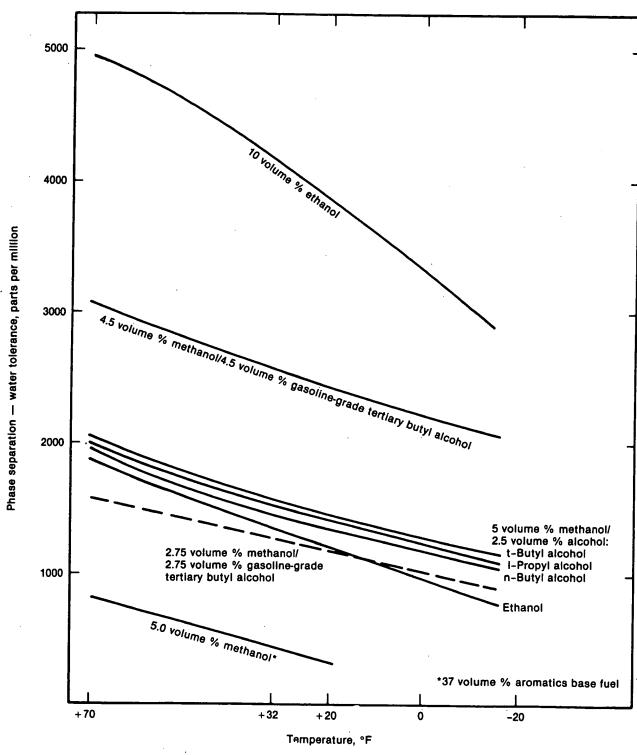
concentration, appears to be independent of temperature. An effective cosolvent increases water tolerance at all temperatures. Chapter 7 addresses water tolerance and separation in gasoline distribution systems.

Oxygenate Effects on Volatility

Methanol is a single compound that boils at 149°F. Ethanol is also a single compound and boils at 172°F. MTBE boils at 131°F. Gasoline, on the other hand, is a mixture of compounds that boils over a range of temperatures (generally 80–437°F). Thus, methanol and ethanol and the other oxygenates have constant volatilities, while the volatility of gasoline can be tailored over a range by adjusting the relative amounts of different hydrocarbons in the mixture. The difference in volatility between the oxygenates and gasoline is an important factor in the performance of gasoline-oxygenate blends in automobile engines with respect to starting, warmup, vapor lock, and other driveability characteristics. These effects are covered in detail in Chapter 4.

Adding alcohols to hydrocarbons or gasoline depresses the boiling temperature of individual hydrocarbons.[31] The effect of alcohol addition on the shape of a distillation curve is shown in Figure 8.[32] The light alcohols cause significant reduction in the temperatures for evaporation of the front end, which affects primarily the first 50 percent evaporated. Alcohols depress the boiling point of aromatic hydrocarbons slightly less than aliphatic hydrocarbons. Lower molecular weight alcohols have the greatest effect on boiling point depression. Methanol causes the largest changes; its effects can be observed even when accompanied by a cosolvent. Higher molecular weight alcohols such as TBA and ethers such as MTBE exert smaller changes on the distillation characteristics.
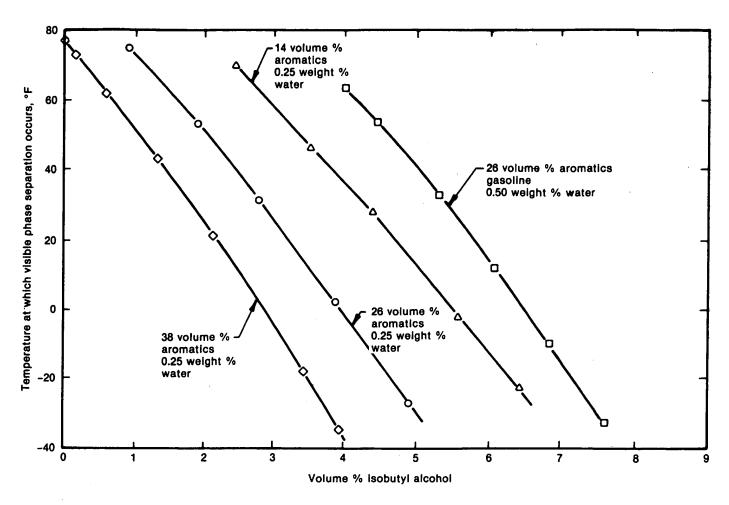
Vapor pressure is another important volatility parameter of gasoline that is adversely affected by the addition of alcohol. A common technique for measuring this parameter is the Reid Vapor Pressure (RVP) method, which involves determination of pressure in a closed chamber maintained at 100°F. As shown in Table 1, the RVP values listed for neat alcohols, ranging from 1.3–4.6 pounds per square inch (psi), appear low relative to that of motor gasoline with RVP values of 8–15 psi. However, blending alcohol into gasoline forms a nonideal solution that does not follow linear blending relationships. Rather than lowering vapor pressure, methanol and ethanol cause increases in RVP as illustrated in Figure 9.[32] Methanol, at very low concentrations, typically generates an increase in RVP of 3 psi. Considering molecular polarity, the plateau-shaped

Figure 6—Water Tolerance of Gasoline-Alcohol Blends

Notes:
1. Indolene base fuel — 30 percent aromatics.
2. Source: References 22 and 30.

Source: Reference 26.

Figure 7—Effect of Cosolvent and Aromatics Content
on Phase Separation of Blends With 10 Volume Percent Methanol

curve suggests that methanol vapors may exist in concentrations disproportionate to the alcohol concentration in the blend. Equal amounts of a cosolvent, such as TBA, blended with methanol mitigate the effect of methanol somewhat but still result in an RVP increase of over 2 psi. Ethanol produces RVP changes of about 1 psi in a 9 psi RVP gasoline, while TBA and MTBE have little effect on gasoline at this RVP level.

When methanol or ethanol is added, gasolines with lower vapor pressures incur larger increases in vapor pressure than gasolines with high vapor pressures. Figure 10 shows that the vapor pressure effect of methanol or ethanol on gasoline with 13 psi RVP is less than it is on a 9 psi RVP gasoline.[31, 33] A partial explanation for this effect is that the alcohol mole fraction at the 10 volume percent level is lower in the 13 psi RVP blend than it is in the 9 psi RVP blend, since the 13 psi RVP

blend, with its higher concentration of lower molecular weight hydrocarbons, contains more moles per unit volume. The RVP increase is a function of alcohol mole fraction.

When gasoline-alcohol blends are commingled with gasoline, as they might be in routine product handling, the effects of the alcohol in the blend are similar to those discussed above.[34, 35] Figure 11 shows that mixing gasoline-alcohol blends with gasoline of the same RVP results in substantially increased vapor pressure. This is due to the non-linear relationship between RVP increase and alcohol concentration over the concentration range of alcohol found in gasoline-alcohol blends and commingled product. The greatest increases in vapor pressure occurred in mixtures that contained about 20 percent of the gasoline-alcohol blend. The blend containing MTBE did not show increased vapor pressure.
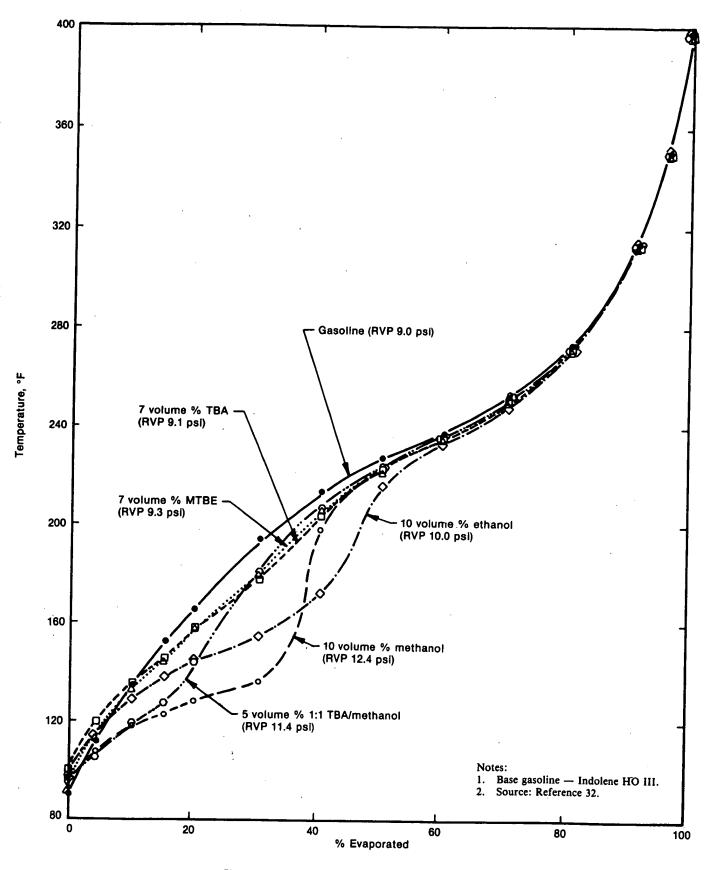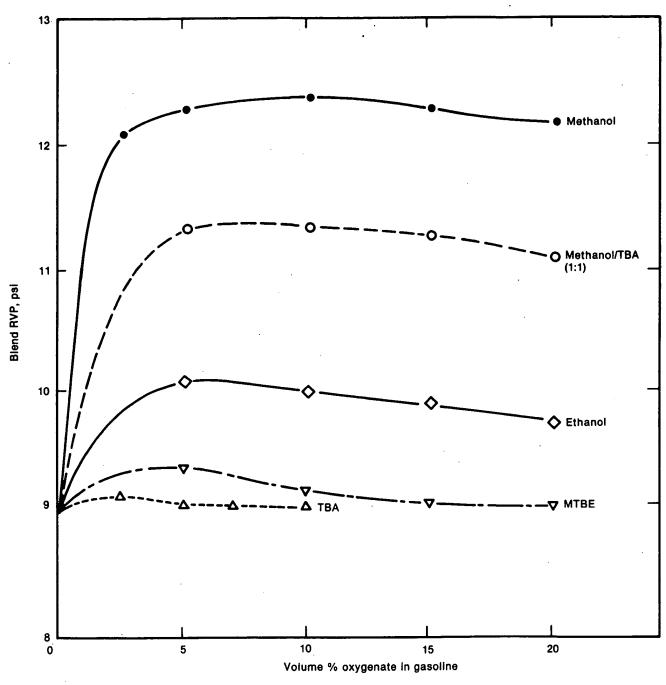
Figure 8—Effect of Oxygenates on Distillation

Notes:
1. Base gasoline — Indolene HO III.
2. Source: Reference 32.

Figure 9—Effect of Oxygenate Concentration on Blend Vapor Pressure

Source: References 31 and 33.
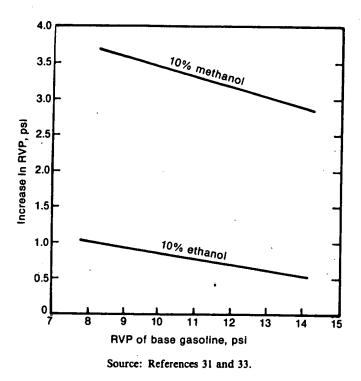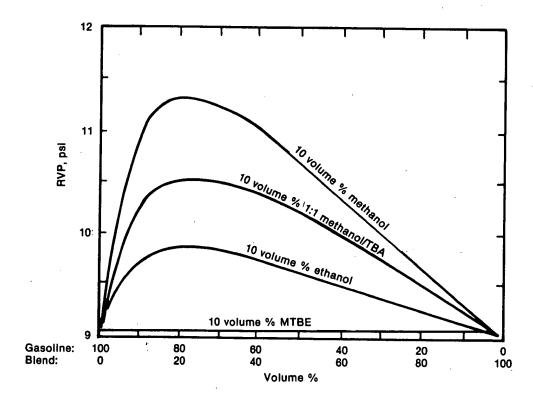
Figure 10—Effect of Base Gasoline RVP on RVP Boost Due to Alcohol Addition

Excessive vapor pressure may increase vehicle vapor lock and evaporative emissions as discussed in detail in Chapter 4. A gasoline volatility parameter, known as Vapor/Liquid (V/L) ratio, is a useful predictor of gasoline performance in a vehicle fuel system at high temperatures. The V/L ratio can be measured or it can be calculated for gasolines using a combination of distillation and vapor pressure characteristics.

Calculations of temperatures for specific V/L ratios of gasoline-alcohol blends using ASTM procedures developed for gasolines do not predict measured values. Figure 12 shows that the correlation of calculated versus measured temperatures for a V/L ratio of 20 ($T_{V/L=20}$) for gasoline and gasoline with MTBE is quite good.[36]

Figure 13 shows how the addition of butane and alcohols changes the temperatures at which various V/L ratios occur. Higher temperatures for a given V/L ratio indicate better hot fuel handling properties. For example, the reference gasoline reaches a V/L ratio of 20 (the ratio that correlates best with vapor lock performance for most cars) at a temperature of 160°F. Adding 5 percent butane to the reference gasoline reduces the $T_{V/L=20}$ to 138°F, which is, coincidentally, the same

Source: Reference 35.

Figure 11—Effect of Commingling a Gasoline and a Gasoline-Oxygenate Blend of the Same RVP

1	Unleaded gasoline
2	10 volume % MTBE
3	10 volume % ethanol
4	10 volume % 1:1 methanol/GTBA
5	10 volume % methanol

Source: Reference 36.
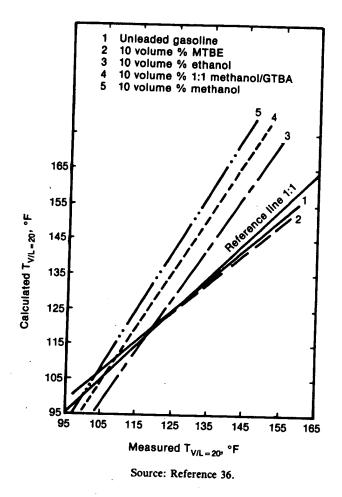
Figure 12—Calculated Versus Measured
Temperature for a Vapor to Liquid
Ratio of 20 $(T_{V/L=20})$

temperature caused by the addition of 10 percent ethanol. Methanol causes a large decrease in the $T_{V/L=20}$ at concentrations as low as 2 percent. In practice a gasoline-methanol blend can be adjusted to achieve the same vapor-locking tendency as a base gasoline by removing all of the butanes and reducing the pentanes. However, doing so would negate the increase in gasoline volume or octane obtained by adding methanol and would still give a distillation curve with a prominent flat segment that could adversely affect vehicle driveability characteristics other than vapor lock — for example, cold-start driveability.

Gasoline-alcohol blends have unusual distillation curves and vapor pressures, and current performance assessment correlations developed with gasoline are not reliable. Chapters 4 and 5 will expand on the significance of the physical and thermal properties of alcohols and ethers on vehicle performance.
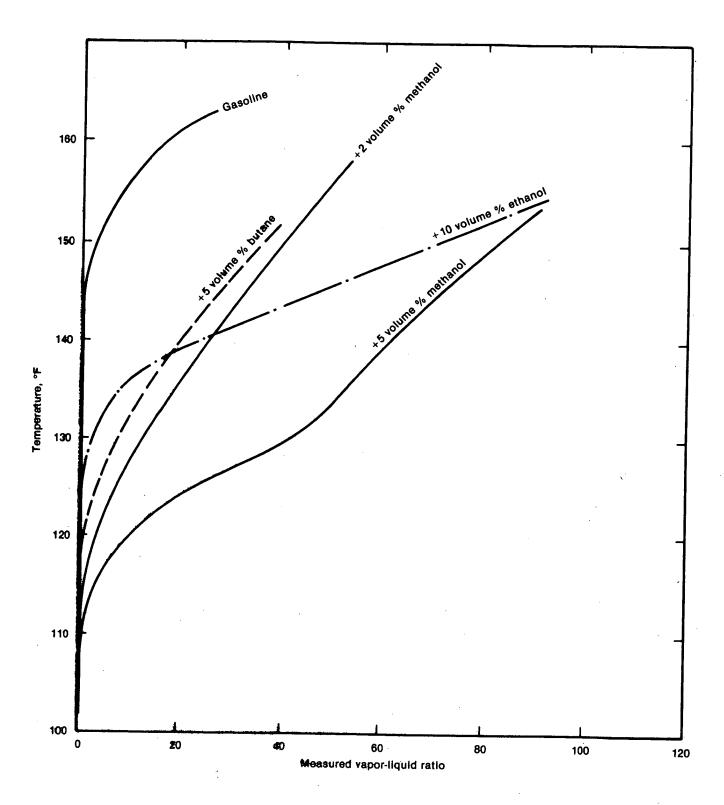
CHAPTER 3—OXYGENATES PRODUCTION TECHNOLOGY, CAPACITY, AND COSTS

Methanol

Worldwide methanol capacity in 1988 is about 440 thousand barrels per calendar day or 6.6 billion gallons per year. U.S. and Canadian capacities are about 110 and 42 thousand barrels per calendar day (1.6 billion and 650 million gallons per year), respectively. The major U.S. and Canadian producers of methanol are Borden, DuPont, Lyondell, Celanese, and Alberta Gas.[37] For perspective, U.S. consumption of gasoline and highway diesel fuel is 8400 thousand barrels per calendar day or 130 billion gallons per year.

Essentially all methanol worldwide is produced from natural gas. Technology also exists to manufacture methanol from coal, cellulosic refuse, or most types of

biomass.[38] In methanol production the feedstock is used to prepare a synthesis gas, either through reforming or catalytic partial oxidation. The synthesis gas is reacted over a catalyst at the proper pressure and temperature to produce methanol. The methanol is then dried and purified.

Natural gas requires little preparation for producing the synthesis gas. Other feedstocks, including coal, have to be sorted, screened, and pulverized before the synthesis gas step. Feedstocks other than natural gas also contain sulfur that has to be removed from the synthesis gas. Since natural gas often contains little sulfur, there may be no need for sulfur removal when natural gas is used as the feedstock. Figure 14 is a simplified diagram of the methanol production process.

Figure 13—Effect of Alcohols and Butane on Measured Vapor to Liquid Ratio

```
┌─────────────────┐     ┌─────────────┐
│ Coal, cellulosic │     │ Natural     │
│ refuse, or biomass│     │ gas         │
└─────────────────┘     └─────────────┘
        │                      │
        ▼                      ▼
┌─────────────┐   ┌─────────────┐   ┌─────────────┐   ┌─────────────┐
│ Feedstock   │──▶│ Synthesis gas│──▶│ Methanol    │──▶│ Distillation │
│ preparation │   │ preparation  │   │ synthesis   │   │ and cleanup  │
└─────────────┘   └─────────────┘   └─────────────┘   └─────────────┘
                                                              │
                                                              ▼
                                                      ┌─────────────┐
                                                      │ Methanol    │
                                                      └─────────────┘
```

Figure 14—Methanol Production Process — Simplified Diagram

Most methanol industry analysts believe that existing worldwide methanol manufacturing capacity will be used just to supply traditional chemical markets and to supply the rapidly growing requirements for the manufacture of MTBE. A massive methanol plant construction program would be required to support supply of fuel to vehicles designed to operate on 85–100 percent methanol.[39] An industry-government cooperative study is underway to develop methanol plant investment costs for fuel grade methanol at various sites throughout the world and to estimate the potential for cost savings through technological advances.

The authors of recent articles on methanol operating and plant capital costs have concluded that they depend strongly on a number of factors.[39, 40, 41] These factors include technology employed, plant size and location, infrastructure needed, return on investment required, and type and cost of feedstock. In every case, the capital charge is a major part of the total cost of methanol. For example, Wagner and Tatterson estimated capital costs to build a new methanol plant that uses natural gas feedstock to be $250–260 million for a 300 million gallon per year plant on the U.S. Gulf Coast or in the Middle East producing methanol with st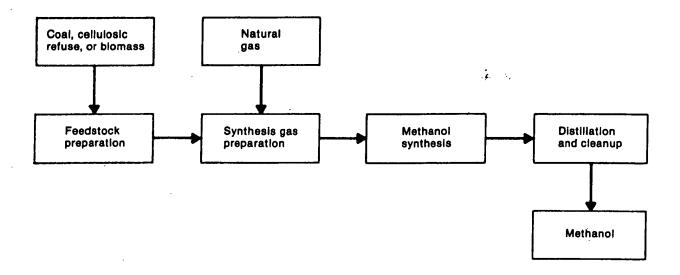ate-of-the-art technology.[41] Wagner and Tatterson estimated capital to fund a new methanol plant that uses coal as feedstock to be about $900 million. The coal plant also incurs extra cost because of the additional facilities required for handling and preparing the feedstock and cleaning up the synthesis gas. Beyaert estimated capital costs of $490–650 million for world-scale plants in remote loca-

tions producing chemical grade methanol using natural gas feedstock and proven technology.[39] Beyaert estimated that a world-scale methanol plant at Prudhoe Bay, Alaska, would even exceed this range, costing approximately $815 million.

Feedstock costs can be highly variable. Estimated costs for natural gas feedstock can range from less than $1.00 (the price of flared gas in remote locations is very dependent on local factors) to the current market price of $2.00 per million British thermal units (Btu) for U.S. natural gas on the Gulf Coast, which is also the estimated price for some undeveloped remote locations.

The return on investment (ROI) required affects methanol production cost significantly, and most recent studies have assumed about 15 percent. Some methanol producers might be willing to build plants yielding lower ROI; however, others might expect 15 percent or more ROI, depending upon the availability of alternative investments, perception of risks, and government incentives. A more substantial return might be required to justify plant investment in risky ventures or in a politically unstable country.

Table 5 shows estimates by Beyaert of long-term methanol costs delivered to the U.S. West Coast from new plants in the Middle East and Australia.[39] Capital costs are based on reported and estimated costs to build chemical grade methanol plants at various locations around the world from 1981–1987. The costs include factors for building in developed and undeveloped remote locations and assume an after tax ROI of 15 per-

Table 5—B. Beyaert Estimates: Costs of Methanol From New Plants Delivered to the U.S. West Coast, 292 Million Gallons Per Year Capacity

	Special[b] Situation	Standard Economics	
		Low End	High End
Capital investment, $ million	416	490	650
Location	Saudi Arabia (developed site)	Saudi Arabia (developed site)	Australia (undeveloped site)
Construction cost factor versus U.S. Gulf Coast	1.39	1.39	1.44

	Dollars per gallon of methanol		
Feedstock and fuel			
Gas at $0.50 per million Btu	0.05	0.05	—
Gas at $2.00 per million Btu	—	—	0.20
Operating costs	0.10	0.10	0.12
Capital charges (15% ROI, constant $)	0.24[b]	0.43	0.57
Transportation to U.S. West Coast	0.11	0.11	0.08
Total cost of methanol	0.50	0.69	0.97
Mileage adjusted gasoline equivalent (1.8 gallons of methanol = 1 gallon of gasoline)	0.90	1.24	1.75

Notes:
[a]Source: Reference 39.
[b]Special situation assumes lower construction costs due to depressed conditions in the construction and ·fabrication industries and 10 percent ROI due to low cost loans by some foreign governments with excess natural gas. B. Beyaert concluded that there are not likely to be enough of these special situations to determine market prices for methanol but that market price will be determined by the marginal producer.

cent above inflation. The costs, however, do not consider recent developments in methanol production technology such as advances in steam reforming and catalytic partial oxidation, which might lower investment costs. Feedstock and fuel costs (natural gas) are site specific and range from 5 to 20¢ per gallon methanol.

Table 6 shows estimated costs by Wagner and Tatterson to produce fuel grade methanol from natural gas in plants on the U.S. Gulf Coast and a developed site in the Middle East.[41] The plants employ advances in steam reforming and catalytic partial oxidation technology, and natural gas is valued at $0.75 for the remote site. In this case Wagner and Tatterson assume a 15 percent after tax ROI (10 percent ROI above 5 percent inflation), and transportation for the remote site is to the U.S. Gulf Coast, not the West Coast.

There is insufficient natural gas in the lower 48 states to supply methanol-based transportation fuels in addition to residential, commercial, and other current uses

without increasing natural gas prices substantially. Therefore, future methanol plants that would supply methanol as a transportation fuel would be built in locations where natural gas is relatively inexpensive due to remoteness from markets.

The energy balance for the production of methanol is shown in Table 7. In methanol manufacture natural gas serves as both feedstock and the source of process energy; therefore, the energy balance is simple. The methanol produced contains about 65 percent of the energy contained in the natural gas consumed by the plant. The 35 percent loss of energy can be viewed as the penalty for liquefying the gas to methanol.

The primary economic consideration in the use of methanol as motor fuel is the cost. Based on the above methanol cost estimates and using the gasoline mileage equivalency factor of 1.8 (see Chapter 2), the delivered cargo cost for an amount of methanol equivalent to one gallon of gasoline would range from $0.77 to $1.75.

Table 6—T. O. Wagner and D. F. Tatterson Estimates: Costs of Methanol From New Plants Delivered to the U.S. Gulf Coast, 300 Million Gallons Per Year Capacity

Feedstock	Natural Gas	Natural Gas	Coal
Site	U.S. Gulf Coast	Middle East (developed site)	U.S.
Capital investment, $ million	250	260	900
Construction cost factor versus U.S. Gulf Coast	1.00	1.04	1.00

	Dollars per gallon of methanol		
Feedstock and fuel:			
Gas at $2.00 per million Btu	0.16	—	—
Gas at $0.75 per million Btu	—	0.06	—
Coal at $30 per ton[b]	—	—	0.15
Operating cost	0.08	0.09	0.25
Capital charges (15% ROI)[c]	0.19	0.20	0.58
Transportation to U.S. Gulf Coast	0	0.08	(0.02)[d]
Total cost of methanol	0.43	0.43	0.96
Mileage adjusted gasoline equivalent (1.8 gallons of methanol = 1 gallon of gasoline)	0.77	0.77	1.73

Notes:
[a]Source: Reference 41.
[b]Midwest coal, or Western coal including freight.
[c]10 percent ROI above 5 percent inflation.
[d]Reflects manufacture closer to market than U.S. Gulf Coast.

These costs are far above the price needed to be competitive with gasoline. The first quarter 1988 U.S. Gulf Coast spot cargo price for gasoline was $0.45 to $0.50 per gallon. Accordingly, unless crude prices more than double, massive government subsidies are granted, or significant advances in production technology are developed, methanol cannot compete with gasoline.[42]

Table 7—Energy Balance for Production of Methanol

	MBTU Per Gallon of Methanol
Feedstock and process energy (natural gas)	88
Energy in product	57
Overall efficiency, percent	65

Source: Reference 39.

With today's technology, methanol from plants using cellulosic refuse or biomass for feedstocks would be at least as expensive as methanol produced from coal.[43] Costs for collection and transportation of the raw materials are high and very site specific.

Ethanol

Current U.S. fuel-ethanol capacity is about 1 billion gallons per year or 65 thousand barrels per calendar day. Major U.S. suppliers are Archer Daniels Midland with 600-million gallons per year (39 thousand barrels per calendar day), Pekin Energy Company with 70 million gallons per year (4.5 thousand barrels per calendar day), South Point Ethanol with 60 million gallons per year (4 thousand barrels per calendar day), New Energy Company of Indiana with 50 million gallons per year (3.3 thousand barrels per calendar day), and A. E. Staley with 40 million gallons per year (2.6 thousand barrels per calendar day).[44]

Over 90 percent of the fuel ethanol in the United States is produced from corn. A bushel of corn yields 2.5 gallons of ethanol. The remainder is produced from other grains such as barley and waste sugars.

In the United States ethanol is produced by either dry-milling or wet-milling processes.[45] In the wet-milling process water is added to the grinding step. The choice between the two processes depends largely on the ability of manufacturers to market by-products. The major by-product of the dry-milling process is distillers dried grain and solubles (DDGS), which is sold in competition with soybean meal as animal feed. By-products of the wet-milling process include gluten feed, gluten meal, and corn oil. Gluten feed is sold as livestock feed; gluten meal is used to make poultry feed.

After milling, starches from the corn are converted by enzymes to fermentable sugars. The sugars are then fermented with yeasts, and the by-products are separated and dried. The low-proof beer from fermentation is distilled to yield 190-proof ethanol, which is further dried and purified to yield essentially 200-proof ethanol. Figure 15 is a simplified diagram of the ethanol production process.[38]

Table 8 shows the costs of manufacturing ethanol from corn for three cases: dry milling in a small plant, dry milling in a large plant, and wet milling in a large plant.[46] More than two-thirds of the ethanol in the United States is produced by wet milling in a few relatively large plants, but many of the plants in operation are small and use dry milling.

As shown in Table 8,[46] the full cost of ethanol after by-product credits, at first quarter 1988 corn and by-product prices, is about $1.90 per gallon for the small dry-milling plant. The costs are about $1.10 and $1.00, respectively, for the large dry- and wet-milling plants. These costs apply to new, undepreciated plants. Without capital recovery the costs fall to about $0.70 and $0.55, respectively. In some cases variable costs may be even lower for large, fully depreciated plants; variable costs as low as $0.35 per gallon have been quoted. Additional ethanol capacity has been obtained by expanding existing large wet-milling facilities, and these plants may carry only a small part of the capital charges shown. As shown in Table 8, feedstock costs are a major factor in the production of fuel ethanols.[46, 47] A change in the
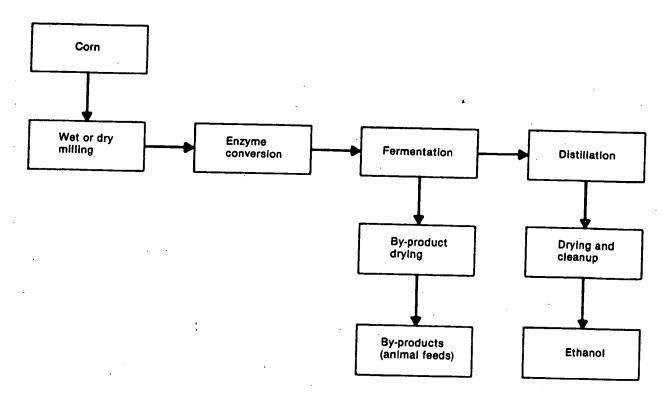

Figure 15—Ethanol Production Process — Simplified Diagram

Table 8—Costs of Ethanol Production

	Dry Milling		Wet Milling
Capacity, million gal/yr:	10	50	50
Capital investment, $ million	41	116	133

	Dollars per gallon of ethanol		
Production costs:			
Corn at $2.00/Bu[b]	0.74	0.74	0.75
Yeast and chemicals	0.11	0.11	0.03
Utilities	0.09	0.09	0.12
Fixed plant costs	0.79	0.28	0.32
Capital charges at 10% ROI, no inflation	0.67	0.38[c]	0.44[c]
Total	2.40	1.60	1.66
By-product credits:			
DDGS $145/ton	0.50	0.50	—
Gluten feed $120/ton	—	—	0.34
Gluten meal $295/ton	—	—	0.19
Corn oil $0.22/lb	—	—	0.13
Total cost of ethanol	1.90	1.10	1.00

Notes:
[a]Source: Reference 46.
[b]These estimates have been adjusted to reflect First Quarter 1988 corn and by-product prices. A change in the corn price of $1.00 per bushel will affect variable costs of ethanol by $0.30 per gallon.
[c]A 15 percent ROI increases capital charges for dry-milling and wet-milling plants by $0.15 and $0.20 per gallon, respectively.

corn price of $1.00 per bushel will affect the variable costs of ethanol by $0.30 per gallon. The capital charge in the cost analysis assumes a 10 percent ROI with no inflation. The 10 percent ROI reflects current market values for ethanol and ethanol plant construction costs. If there is a significant increase in these variables, or if inflation erodes the ROI, then capital charges have to be raised accordingly. For example, a 15 percent ROI with no inflation would increase the capital charges in the cost analysis for the large dry-milling and wet-milling plants by $0.15 and $0.20 per gallon, respectively.

The energy balance in ethanol manufacture, as shown in Table 9,[46] is complicated because of the way feedstock energy is evaluated and because the plant uses different sources for process energy. The plant also generates by-products. The corn feedstock has calorific energy. However, since the corn is not burned directly for fuel, the plant should not be charged for the energy content of the corn as received but rather for the energy needed to grow the corn (that is, the natural gas and distillates for fertilizer and pesticide manufacture; diesel fuel for cultivation, harvesting, and transportation; and

distillates or LPG for corn drying). In good land 33 thousand Btu of energy are typically needed to produce 1 gallon of ethanol. In marginal land or land that must be irrigated, the amount of energy needed can be substantially higher. Process energy of 57 thousand Btu per gallon is needed to grind, cook, convert, and ferment the corn and to distill and dry the ethanol. Most large ethanol plants use coal for process fuel, but smaller

Table 9—Energy Balance for Production of Ethanol

	MBTU Per Gallon of Ethanol
Feedstock (corn)	33
Process energy	57
By-product credit	-10
Total	80
Energy in product	76
Overall efficiency, percent	95

Source: Reference 46.

plants generally use gas, distillate, or residual fuel. Finally, a credit is given for the by-products that equals the energy needed to produce the same amount of animal feed using the most efficient alternative method, which is growing soybeans. No credit is given for refinery energy savings because essentially all ethanol is added downstream, usually at terminals, to fully refined and finished gasoline. This method for producing gasoline-ethanol blends is not expected to change in the foreseeable future. Thus, a total of 80 thousand Btu is consumed to produce a gallon of ethanol that contains 76 thousand Btu for an overall efficiency of 95 percent.

In comparison the efficiency with which crude oil can be converted to liquid fuels is somewhere between 600 and 800 percent. Exploration, production, transportation, and refining typically consume only 12–15 Btu that produces 100 Btu from the crude. The energy used to make hydrocarbon fuels is only a small fraction of the energy in the crude.

Ethanol can also be produced from cellulose or biomass such as wood, corn stover, and municipal solid wastes, but the processes that use these resources involve serious technical and economical problems. For example, cellulose is difficult to dissolve and hydrolyze, and the sugars produced are not fermentable with normal yeasts. Also, because of the low value density of the raw materials, supply and front-end processing must be done on a major scale. This means that processing plants must be very large and therefore would require large capital investments. Furthermore, lignin, which is a partially polymerized phenolic resin, is a major by-product of ethanol production from cellulose, and there is no ready market for this material.

Universities and government laboratories are currently conducting developmental work on processes to convert cellulose to ethanol.[48] The Tennessee Valley Authority (TVA) is operating a 2-ton per day pilot plant, but there is no commercial application or private-sector research. Continued academic research is expected to lead to additional pilot plants; however, full-scale commercial production is not expected in the forseeable future unless valuable uses for lignin and other by-products are found.

Fuel-ethanol production can be put into perspective by considering that, with the cost of ethanol produced from grain at $1.00–1.10 per gallon in a new plant, and first quarter 1988 gasoline Gulf Coast wholesale prices of about $0.45–0.50 per gallon, ethanol manufacture in new plants will continue to depend on federal and state subsidies. In the absence of subsidies only ethanol produced in fully depreciated plants that only support

variable costs may compete with gasoline. In regard to the energy balance ethanol manufacture in a plant that makes maximum use of coal can be viewed as a way of converting solid fuel to liquid energy, but the cost of the conversion is high.

Other Alcohols

ISOPROPYL ALCOHOL (IPA)

North American IPA production is estimated at 30 thousand barrels per calendar day (460 million gallons per year). Major producers are Shell, Exxon, and Union Carbide. IPA is produced by acid catalyzed hydration of propylene. Essentially all IPA produced in North America is used as a chemical feedstock for acetone production or as a solvent. It is usually too expensive to use as a gasoline blending component; however, IPA has been used in gasoline at 2 percent or less to prevent carburetor icing.[49, 50]

BUTYL ALCOHOLS

Tertiary Butyl Alcohol (TBA)

Worldwide capacity of TBA is estimated at 14.5 thousand barrels per calendar day (220 million gallons per year). A total of 13.5 thousand barrels per calendar day (205 million gallons per year) is produced by ARCO Chemical Company as a co-product of propylene oxide production; 10 thousand barrels per calendar day (150 million gallons per year) is produced in the United States, and 3.5 thousand barrels per calendar day (55 million gallons per year) is produced in Western Europe. The remainder is produced in the Far East and Europe by direct hydration of isobutylene. In the United States there is currently no market for TBA to be used by itself as a gasoline blending component, and all TBA available for fuel use is being converted to isobutylene for MTBE production.[49, 50]

Other Butyl Alcohols

Butyl alcohols other than TBA (that is, iso-, normal, and secondary butyl alcohol) are highly valued chemical feedstocks and solvents and are therefore not used as gasoline components. Iso- and normal butyl alcohol are produced from by-product propylene. North American capacity for both iso- and normal butyl alcohols is about 20 thousand barrels per calendar day (300 million gallons per year). Union Carbide and Celanese are the large producers. Secondary butyl alcohol is produced by hydration of butylene. The North American capacity is estimated at 1 thousand barrels per calendar day (15 million gallons per year). Shell, Exxon, and ARCO are major producers.[50]

Methyl Tertiary Butyl Ether (MTBE)

Current worldwide MTBE capacity is about 115 thousand barrels per calendar day (1.7 billion gallons per year).[51] U.S. capacity is estimated at 88 thousand barrels per calendar day (1.3 billion gallons per year). ARCO Chemical and Texas Petrochemical are the major merchant producers with capacities of 42 thousand barrels per calendar day (630 million gallons per year) and 14 thousand barrels per calendar day (200 million gallons per year), respectively. Worldwide capacity of MTBE is expected to expand by about 80 thousand barrels per calendar day (1.2 billion gallons per year) during the next several years, including about 22 thousand barrels per calendar day (330 million gallons per year) increase for the United States.[52, 53, 54] Large plants are planned for Europe and the Middle East to supply the European demand anticipated by lead phasedown. Some of the MTBE produced in the Middle East may reach the United States.

MTBE is produced by reacting isobutylene with methanol over an acid catalyst.[55] Major sources of the isobutylene feedstock are derived from catalytic cracking and ethylene cracking; isobutylene is a by-product of these processes and its supply is therefore limited.

While MTBE production has depended largely upon the availability of isobutylene from refinery operations, isobutylene is available from other sources. For example, isobutylene is currently being produced by dehydrating tertiary butyl alcohol (TBA). Also, at higher costs isobutane can be dehydrogenated to isobutylene; mixed butenes can be isomerized to isobutylene; or mixed butanes can be isomerized to isobutane and then dehydrogenated. These processes are expensive, and only the isobutane-to-isobutylene process has seen limited commercial use in the United States.

Table 10 shows MTBE production costs for new plants.[56] Capital charges assume a 15 percent ROI with no inflation and are based on the market value of MTBE and construction costs for MTBE plants in the first quarter of 1988. The costs are also based on Gulf Coast prices for feedstocks in early 1988.

The cost to produce MTBE from by-product isobutylene is thus between 53 and 58¢ per gallon. Using butanes, which have to be converted to isobutylene as the feedstock, raises the cost of MTBE to between 71 to 75¢ per gallon because of the high capital costs required for the conversion facilities.

Table 10—Costs of MTBE Production

Feedstock	Isobutane	Mixed Butanes	Steam Cracker Butylenes	Fluid Cracker Butylenes
Capacity—MBSD:[b]	10	10	5	2.5
Capital investment $ million	100.0	130.0	14.0	10.5

	Cents per gallon of MTBE			
Raw materials:				
Isobutane at 29.6¢/gal	28.4	—	—	—
Mixed butanes at 26.6¢/gal	—	24.8	—	—
Isobutylene at 36.5¢/gal	—	—	28.9	28.9
Methanol[c] at 50¢/gal	17.0	17.0	17.0	17.0
Utilities	2.2	2.7	0.7	1.7
Labor and overhead	2.1	2.4	0.8	1.1
Maintenance, taxes, and insurance	4.2	5.4	1.2	1.7
Capital recovery	17.4	22.4	4.8	7.2
Total cost of MTBE	71.3	74.7	53.4	57.6

Notes:
[a]Source: Reference 56.
[b]MBSD = Thousand barrels per stream day, 330 stream-days per calendar year.
[c]A change in the methanol price of 10 cents per gallon will affect raw materials costs of MTBE by about 3.4 cents per gallon.

Other Ethers

TERTIARY AMYL METHYL ETHER (TAME)

TAME is produced via the MTBE process using a feedstock that contains isoamylenes as well as isobutylene.[49] The result is a mixed product of MTBE and TAME. Plants that produce these products are limited to refineries for in-house use; that is, there is no merchant MTBE/TAME available. Also, plants are relatively small and use refinery-specific by-product streams for feedstock.

ISOPROPYL ETHER (IPE)

IPE is a by-product of isopropyl alcohol production. Its availability is less than 1 thousand barrels per calendar day (15 million gallons per year), and fuel use has been limited to oil companies that are affiliated with

chemical companies that produce isopropyl alcohol.[57] Special procedures are used to handle and store neat isopropyl ether.[58]

ETHYL TERTIARY BUTYL ETHER (ETBE)

Very recently, ETBE has been proposed as a means for expanding the range of available oxygenates which have favorable octane and volatility blending characteristics, as well as the advantage of pipeline fungibility. ETBE can be made by reacting isobutylene with ethanol over a catalyst. While no commercial plant manufactures ETBE today, ETBE plants are expected to closely resemble present MTBE plants. Although ETBE seems to have very good blending properties, the economics of production appear to be dominated by the cost of ethanol.[275] However, most of the research needed to detail the production, blending value and environmental characteristics of ETBE still remains to be completed.

CHAPTER 4—ALCOHOLS AND ETHERS BLENDED WITH GASOLINE

Gasoline-Oxygenate Blends: Attractions and Concerns

The major attractions of oxygenated blends in automotive applications are a) octane improvement, b) reduction of exhaust carbon monoxide (CO) and hydrocarbons (HC), and c) potential additional energy resources as automotive fuel.

However, there are concerns about the use of oxygenated blends. These include a) impaired vehicle driveability, b) increased evaporative emissions, c) increased exhaust emissions of oxides of nitrogen (NO_x), d) compatibility with vehicle fuel system elastomers and metals, e) water tolerance and phase separation, and f) reduced volumetric fuel economy. These concerns are directed mainly at gasoline-alcohol blends and not at gasoline-ether blends. Neither the attractions nor the concerns apply universally throughout the spectrum of vehicles in the United States.

This chapter first describes the current federal constraints on the use of oxygenates in gasoline. Further discussion covers the effects of oxygenated blends on vehicle performance.

Clean Air Act Requirements

Attempts to achieve national goals for improved air quality and energy self-sufficiency often give rise to conflicting solutions. The Department of Energy (DOE) currently considers alcohols to be viable extenders of the U.S. gasoline supply and methanol as an automotive

fuel for the future.[59] The EPA recently mandated the phasedown of lead antiknock compounds in gasoline. The EPA has also proposed restrictions on gasoline vapor pressure, which will result in limitations on the use of butane, a component of high octane blending value. The combination of these EPA regulations forces refiners and marketers of gasoline to consider new ways to restore the lost octane. One approach is to blend oxygenates into gasoline, but this is subject to certain legal and practical limitations.

The EPA is empowered to regulate fuel volatility and any other fuel property which, if uncontrolled, could contribute either directly or indirectly to air pollution. Under Section 211(f) of the Clean Air Act, as amended in 1977, unleaded gasoline marketed for use in vehicles manufactured after 1974 must be substantially similar to those fuels used during the federal emissions certification testing procedures. The EPA was concerned that oxygenated blends could adversely affect exhaust and evaporative emissions control systems. After recognizing the ad hoc commercialization of ethanol blends in 1978, the EPA began to impose restrictions.

The first potential restriction considered by the EPA eventually became a non-restriction. It dealt with gasohol, a blend of one part agriculturally-derived ethanol with nine parts finished gasoline. After the first Arab oil embargo in 1974, gasohol marketing was stimulated by a variety of tax incentives. When the "substantially similar" rule was written into the 1977 Clean Air Act Amendments, the EPA faced a dilemma. Gasohol was

a politically popular fuel that could not technically be construed to be substantially similar to certification gasoline because it contained up to 3.7 percent by weight oxygen. However, the 1977 Amendments to the Clean Air Act provided that the EPA could grant a waiver of Section 211(f) requirements if the applicant demonstrated that the fuel in question did not significantly deteriorate, or contribute to the deterioration of, the performance of any motor vehicle emissions control system.

In 1978 gasohol interests applied to the EPA for a waiver. However, the EPA failed to render a determination of the application within the 180-day period provided for by law, and a waiver was thereby automatically granted for gasohol by operation of the Act. By permitting this automatic waiver, the EPA allowed gasohol blending but reserved its right to enforce Section 211 provisions in the future.

In 1981 the EPA ruled that unleaded fuels blended with oxygenates at concentrations of 2 percent by weight or less oxygen qualified as being substantially similar.[60] All finished blends were required to meet at least one of the seasonal and geographical ASTM D 439 volatility class limits.[33] Some of the test procedures

within the ASTM D 439 specification are considered unsuitable for use with oxygenated fuel blends. ASTM has developed a new specification that includes volatility testing procedures intended to accommodate both gasolines and oxygenated blends. This specification has undergone final approval by ASTM and will be issued as D 4814.[61]

The "substantially similar" rule allowed oxygenates, such as ethanol, propyl alcohols, butyl alcohols, higher molecular weight alcohols, and ethers to be used at volume concentrations proportionate to their respective oxygen contents. Thus, compounds containing less oxygen that were more similar to hydrocarbons in chemical and physical characteristics than methanol could be used at higher volume concentrations. For example, the "substantially similar" rule nominally allows 9 percent by volume butyl alcohol or 11 percent by volume MTBE in a typical gasoline (see Table 11). Methanol blends were excluded from the "substantially similar" rule at concentrations above 0.3 percent by volume because of questions concerning the effects of gasoline-methanol mixtures on fuel system components, water separation, and evaporative emissions.[60] Methanol was allowed at a maximum of 0.3 percent by volume, a level consistent with longstanding commercial applications as a fuel

Table 11—Some Oxygenated Compounds Approved by EPA for Use in Unleaded Gasoline

Compound[a]	Broadest EPA Waiver	Date	Maximum Oxygen, Weight %	Maximum Oxygenate, Volume %
Methanol	Substantially similar	July '81	—	0.3
Propyl Alcohols	Substantially similar	July '81	2.0	(7.1)[d]
Butyl Alcohols	Substantially similar	July '81	2.0	(8.7)[d]
Methyl-tertiary-butyl ether (MTBE)	Substantially similar	July '81	2.0	(11.0)[d]
tertiary-Amyl methyl ether (TAME)	Substantially similar	July '81	2.0	(12.7)[d]
Isopropyl ether	Substantially similar	July '81	2.0	(12.8)[d]
Methanol and butyl alcohol or higher molecular weight alcohols in equal volumes	Substantially similar	July '81	2.0	5.5
Ethanol	Gasohol[b]	1979, 1982	(3.5)[d,e]	10.0
Gasoline grade tertiary butyl alcohol (GTBA)	ARCO	1981	3.5	(15.7)[d]
Methanol + GTBA (1:1 maximum ratio)	ARCO (OXINOL®)	1981	3.5	(9.4)[d]
Methanol @5 volume % maximum + 2.5 volume % minimum cosolvent[f]	DuPont	1985	3.7	[c]
Methanol @5 volume % maximum + 2.5 volume % minimum cosolvent[g]	Texas Methanol (OCTAMIX)	1988	3.7	[c]

Notes:

[a] All blends of these oxygenated compounds are subject to ASTM D 439 volatility limits except ethanol. Contact the EPA for current waivers and detailed requirements, U.S. Environmental Protection Agency, Field Operations and Support Division (EN-397F), 401 M Street, S.W., Washington, D.C. 20460.

[b] See Chapter 4, Clean Air Act Requirements.

[c] Varies with type of cosolvent.

[d] Calculated equivalent for average specific gravity gasoline (0.737 specific gravity @60°F, NIPER Gasoline Report). Calculated equivalent depends on the specific gravity of the gasoline.

[e] Value shown is for denatured ethanol. Neat ethanol blended at 10.0 volume % produces 3.7 weight % oxygen.

[f] The cosolvents are any one or a mixture of ethanol, propyl, and butyl alcohols. Corrosion inhibitor is also required.

[g] The cosolvents are a mixture of ethanol, propyl, butyl and higher alcohols up to octyl alcohol. Corrosion inhibitor is also required.

system de-icer and as a cosolvent for other permitted fuel additives.

The 1979 waiver for gasohol specified 10 percent by volume ethanol, and the "substantially similar" rule permitted between 0 and 5.4 percent by volume. Blends with more than 5.4 percent by volume and less than 10 percent by volume were not covered by exact language until 1982 when the EPA clarified the waiver and permitted concentrations of ethanol up to and including 10 percent by volume. The EPA does not mandate that blends containing up to 10 percent by volume ethanol must meet ASTM D 439 requirements. Thus, the direct addition of up to 10 percent by volume of ethanol to unleaded gasoline can be made at distribution terminals or at other points in the distribution network. EPA allows up to 2 percent by volume of MTBE in the unleaded gasoline to which ethanol is added, if the MTBE is present only as a result of commingling in transport and storage and not purposely added as an additional component. Blending in such manner, without regard for meeting ASTM D 439 specifications for volatility, is commonly referred to as "splash blending."

The effect of splash blending on volatility, illustrated in Figures 8 and 9, is to flatten the distillation curve and increase the RVP approximately 1 psi in blends with 2 to 10 percent by volume ethanol. Few marketers, if any, adhere to ASTM D 439 specifications for their ethanol blends.

The first waiver dealing with methanol concentrations above 0.3 percent by volume was granted to Sun Oil Company in 1979. It allowed the use of 2.75 percent by volume methanol with an equal volume of TBA up to a blend oxygen total of 2 percent by weight oxygen. Sun Oil Company demonstrated that cosolvents, namely higher alcohols, reduced some of the adverse effects of methanol on volatility and water tolerance in blends. ARCO also received a waiver in 1979 to use up to 7 percent by volume TBA, which ARCO had marketed since 1969. These waivers were superseded by the "substantially similar" definition in 1981.

At the request of ARCO the EPA granted a waiver in 1981 for the use of the following blends containing a maximum of 3.5 percent by weight oxygen: a) gasoline-grade TBA (GTBA), and b) OXINOL® , up to 1:1 volume ratio methanol in GTBA. At the maximum permitted level methanol concentration in the finished gasoline blend could be as high as 4.8 percent by volume in typical gasoline. The highest allowable content of an oxygenate listed is 15.7 percent by volume GTBA.

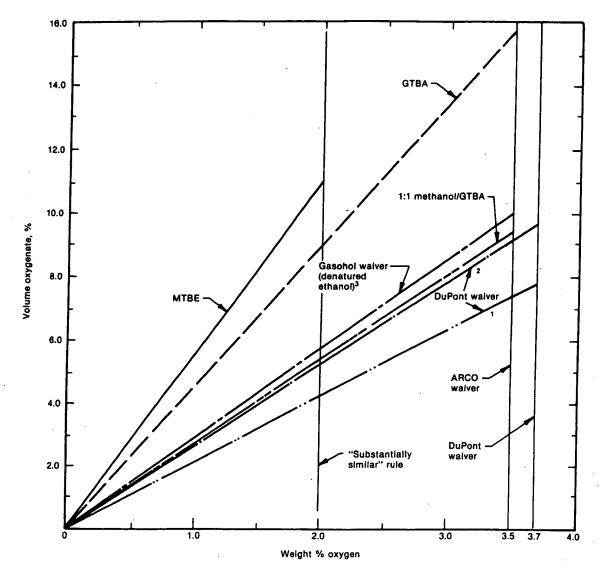Figure 16 shows the relation between percent by weight oxygen and percent by volume oxygenate.

The EPA granted a waiver request submitted by DuPont in 1985 for a maximum of 5.0 percent by volume methanol with at least 2.5 percent by volume cosolvent of ethanol, propyl, or butyl alcohols in the finished blend, up to a limit of 3.7 percent by weight oxygen, accompanied by specific corrosion inhibitors. In addition the waiver incorporated a water tolerance or phase separation requirement.[62]

The EPA's concern in granting this waiver as DuPont requested was the potential effects of the combination of methanol and ethanol on evaporative emissions. Even though previous EPA waivers specified volatility limits according to ASTM D 439 for finished blends, EPA initially required that a special volatility restriction called Evaporative Index (EI) also be imposed before granting the waiver to DuPont in January 1985.[62] Upon petition the EPA subsequently reconsidered and withdrew the EI requirement but emphasized that the ASTM standards be followed rigidly.[63]

Although the EPA has established mandatory compositional limits for unleaded fuel blends, it does not regulate the use of oxygenates in leaded gasolines. A considerable range of formulations of leaded gasolines may, therefore, exist at retail outlets. In addition state laws concerning dispensing pump labeling of gasoline-alcohol blends are not uniform. At least 42 states, however, require labeling of the presence and type of alcohol in the fuel at the pump as a consumer protection measure.[64] Chapter 7 details handling considerations. The remainder of this chapter describes recognized technical effects of oxygenated blends and explains factors that justified the imposed legal limits on blend composition.

Vehicle Technology and Fuel Interactions

The current population of automobiles and trucks in the United States comprises a technological potpourri that has never been more diverse. The impact of government regulations began to change the automobile significantly with respect to fuel concerns about twenty years ago. Federal regulations for emissions (EPA), safety, and fuel economy (Department of Transportation) began with the 1968 models and have steadily become more severe. Due in part to recently lower scrappage rates, the current population of about 130 million passenger cars and light-duty trucks encompasses automotive technology with very different responses to gasoline-oxygenate blends. Unusual vehicle behavior on blends can occur since the vehicles were

Notes:
1. 5 percent volume methanol + 2.8 percent volume ethanol.
2. 5 percent volume methanol + 4.7 percent volume butyl alcohol.
3. Neat-ethanol blended at 10.0 volume percent produces 3.7 weight percent oxygen.

Figure 16—Relationship Between Volume Percent Oxygenate and Weight Percent Oxygen in 0.737 Specific Gravity Gasoline

designed and optimized for gasoline. Some designs are more tolerant of blends than others. This is especially true for vehicles manufactured before 1981.

The EPA, for purposes of emissions assessment, uses the following categories:[65]
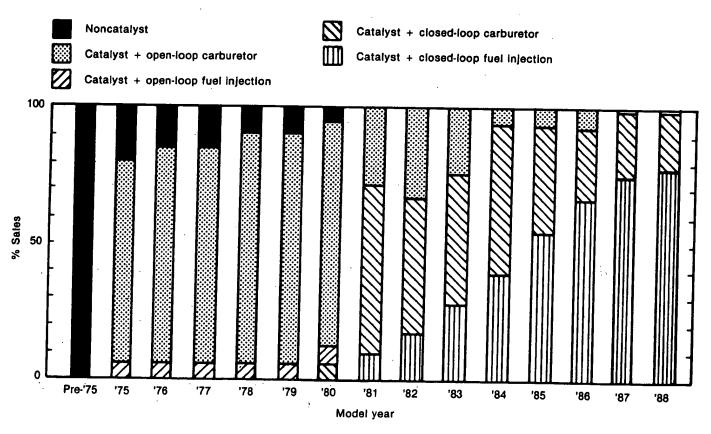
a. Non-catalyst — generally models before 1975; includes pre-emission control cars prior to 1968 (federal), as well as "lean-burn" systems circa 1973-4.

b. Open-loop carbureted — with oxidation-only exhaust catalyst.

c. Open-loop fuel injected — with oxidation-only catalyst.

d. Closed-loop (computer-control) carbureted — with HC, CO, and NO_x catalyst.

e. Closed-loop fuel injected — either central point or port injection with HC, CO, and NO_x catalyst.

About one-third of the light-duty vehicles on the road currently fall into the first group.[66] The presence or absence of a catalyst has no direct effect on vehicle response to blends. However, the design features of the fuel metering system are of great importance. Figure 17 illustrates the change in applied technology during the past fourteen model years. Between 30 and 40 percent of the cars on the road have computer-controlled "closed-loop" fuel systems with three-way catalysts to control HC, CO, and NO_x. Conversely, 60 to 70 percent of the car population remains equipped with "open-loop" fuel metering systems that are not computer-controlled.

The EPA has required vehicle manufacturers to demonstrate that new models comply with emissions regulations while using fuels considered to be representative of those generally available.[67] Manufacturers were not required or allowed to use gasolines blended with oxygenates as certification fuels, even though the sale of oxygenated blends has grown significantly since

the early 1980s. Gasohol sales, for example, reached 8 percent of total gasoline sales during 1985–1986.[59] At the same time consumers became confused about the viability of the gasoline-oxygenate blends available on the market. Automobile manufacturers, both foreign and domestic, presented dissimilar recommendations to new car owners, even though it appeared to the layman that all cars employed similar state-of-the-art technology. For 1987 model year passenger cars, representing the highest level of technology for which statistics have been compiled, automobile manufacturers accounting for over 20 percent of U.S. car sales recommended against the use of blends containing methanol.[68] Vehicle reliability aspects are discussed on pages 50 and 51.

Automobile manufacturers took a cautious approach to ethanol and methanol blends, primarily because emissions certification and warranty experience were based on the use of gasoline. It was assumed that these blends would change vehicle performance because etha-

Source: Reference 65.

Figure 17—Technology Mix — Passenger Car Emissions Control Technology Distribution

nol and methanol modified the physical, chemical, and thermal properties of gasoline. When alcohols are blended into gasoline, they inevitably reduce heating value, increase the heat required for vaporization, change density and viscosity, introduce problems with water separation from the blend, and may accelerate deterioration of elastomers and metals. Some of the property differences directly affect fuel metering rate, mixture preparation before combustion, and the efficiency of combustion.

VEHICLE TECHNOLOGY MIX AND ENLEANMENT EFFECTS OF BLENDS

Vehicle fuel metering systems that have fixed factory calibrations of the rate of fuel delivery in proportion to engine air consumption will respond to physical properties of fuels. These systems are termed open-loop because there is no feedback control to compensate for fuel differences. They can use either carburetion or fuel injection. Carburetors are sensitive to fuel properties because they meter according to internal pressure differentials and generate an emulsion of liquid fuel and air in preparation for discharge. Fuel injection systems are less sensitive to fuel physical properties because they operate at high pressures and are controlled by either mechanical or electrical means.

Conventional carburetors are calibrated on gasoline to deliver an optimum amount of fuel in proportion to volumetric air consumption for three modes of driving: maximum power, cruising, and idling. Mechanical devices, namely choke systems and accelerator pumps, are also built into a carburetor to assist with cold start-

ing and acceleration. Typically, carburetors are manufactured to match the optimized flow calibration to within 3 percent during each driving mode.[69] Deviations in fuel delivery outside the established limits can cause undesirable driveability effects, high exhaust emissions, and poor fuel economy. The fuel-air mixture ratio can change (usually enrichen) from established calibrations in vehicles on the road due to degradation of maintenance factors such as carburetor cleanliness and air cleaner efficiency.

Carburetors vary in response to fuel properties. Basically, carburetor fuel delivery is proportional to fuel density and inversely proportional to viscosity. Although the effects of density and viscosity can be observed when fuels of widely different properties are used, possible effects of blends with oxygenates within the range approved by the EPA have not been reported.

Even though differences in the mass or volumetric metering of blends and gasoline may be insignificant in an open-loop fuel system, the difference between the energy metering rates is important. Because the open-loop carbureted or fuel-injected system delivers blends at about the same weight or volume of blend as gasoline, the net heating value of the fuel charge is less with blends. As Table 12 shows, the waiver for GTBA allows the greatest change in specific gravity, a difference of only 1.2 percent. However, the heating value of blends can be lower than typical gasoline by as much as 4.3 percent on a mass basis or 3.3 percent on a volumetric basis. The deficiency in energy delivery caused by blends can be regarded as thermal "enleanment." The term "enleanment" is used herein to indicate that the com-

Table 12—Heating Value of Some Gasoline-Oxygenate Blends

| | | | Blend | | |
| | | | | Lower Heating Value | |
Oxygenate Component	Specific Gravity @60°F	Btu/lb	Btu/Gal @60°F	Volumetric % Decrease
Base gasoline	0	0.737	18,600	114,100	0
Waiver					
Gasohol	10 vol % ethanol	0.743	17,800	110,300	-3.3
Substantially Similar:					
2.0 weight % oxygen	Propyl alcohol	0.741	18,200	112,200	-1.7
	Butyl alcohol	0.742	18,200	112,400	-1.5
	MTBE	0.738	18,200	111,800	-2.0
ARCO:					
3.5 weight % oxygen	Methanol/GTBA (1:1 ratio)	0.742	17,900	110,500	-3.2
	GTBA	0.746	17,900	111,000	-2.7
DuPont:	5.0 volume % methanol				
3.7 weight % oxygen	+2.5 volume % ethanol	0.741	17,900	110,300	-3.3

bustible component, that is, the hydrogen and carbon content, of the mixture becomes smaller. Enleanment can have desirable or undesirable effects on engine power, fuel economy, or exhaust emissions, depending upon the designed metering calibration.

The magnitude of the thermal enleanment effect is dictated by the engine response to mixture strength and the established calibration settings of the carburetor or fuel injection system. Figure 18 illustrates that engine power and efficiency are optimum at widely different mixture strengths.[70] Enleanment of the mixture from that required for maximum power results in some power loss and, up to the mixture strength for maximum economy, improved engine efficiency. Hypothetically, if the calibration setting were optimized for best fuel utilization and the mixture became leaner, both engine efficiency and power would drop. Generally, open-loop calibrations are set for best economy at part-load, cruise operating conditions. Further enleanment due to a fuel blend, as described above, would cause poorer fuel economy.
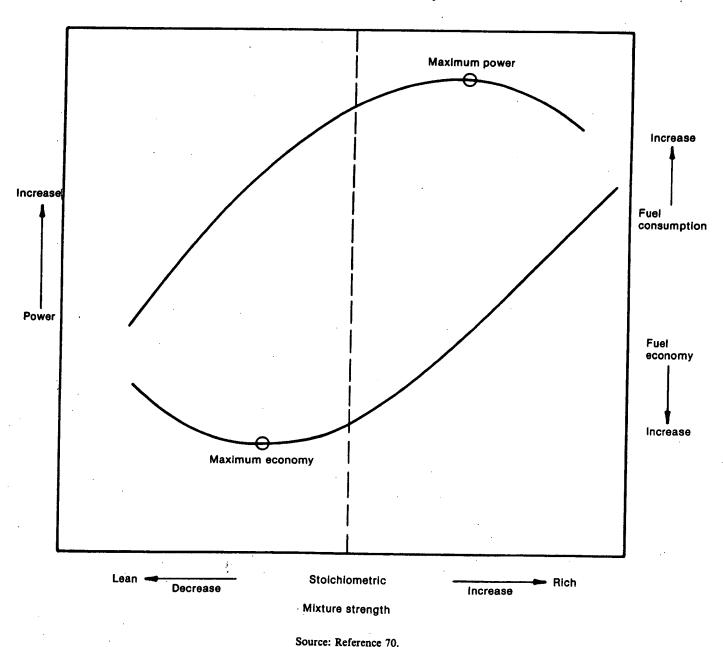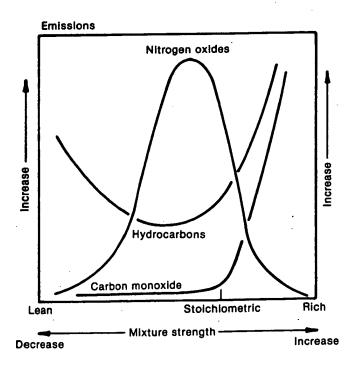

Source: Reference 70.

Figure 18—Effect of Fuel-Air Mixture Strength on Power and Fuel Economy

It is common engineering practice to calibrate wide-open throttle mixture strength very close to that for maximum power. As a result vehicles in heavy duty service with more wide open throttle operation could experience improved fuel economy due to enleanment and reduced available power during the portion of driving conducted at heavy loads. Thus, the effects of blends on the driveability and fuel economy of individual vehicles can be predicted if the calibration point at which the vehicle is to be operated is known. To some extent blend effects can be predicted for different vehicle categories if the nature of the fuel metering system and duty cycle can be characterized. Real world maintenance of vehicles, of course, complicates the situation.

Exhaust emissions are also very sensitive to changes in mixture strength as shown in Figure 19. There are distinctly different mixtures for minimum emissions of HC and for maximum emissions of NO_x. The response curve for CO remains at a minimum value at mixtures leaner than the stoichiometric, that is, chemically correct for complete combustion of the hydrogen and carbon. Gasoline-oxygenate blends can be expected to reduce CO, and to a lesser extent HC, due to mixture enleanment in open-loop vehicles calibrated to operate richer than stoichiometric on gasoline. This benefit of

Source: Reference 71.

Figure 19—Effect of Fuel-Air Mixture Strength on Exhaust Emissions

lower CO and HC, however, could be offset by a corresponding increase in NO_x. At part throttle low load conditions the response curve for NO_x is not as pronounced as illustrated in Figure 19, and the NO_x increase under these conditions may not be greatly affected due to enleanment by blends. Thus, calibration and operating conditions dictate the response of any given vehicle. A wide range of responses to blends has been observed within the car population.

Fuel metering systems that have feedback closed-loop control are designed to maintain engine operation at stoichiometric mixture strength under most driving conditions. These systems typically are deactivated during cold start, initial warmup, and maximum power, so at these times the fuel metering operates in an open-loop mode. In closed-loop mode the feedback control seeks a predetermined oxygen level in the exhaust, and within its range of accommodation fuel flowrate is automatically increased in the correct proportion to compensate for the enleanment inherent in blends. During periods of open-loop operation the system does not correct for the inherent enleanment of blends and operates as calibrated. Some newer closed-loop vehicles are equipped with "adaptive learning." Properly functioning vehicles with adaptive learning continuously adjust their open-loop fuel calibrations based on the most recent period of closed-loop operation. Thus, they can compensate for fuel-caused enleanment even during open-loop operation.

The benefits of closed-loop control extend well beyond those of emissions reduction. Mixture strength (with respect to stoichiometry) stays constant without regard to fuel composition while in closed-loop mode, and driveability and power, therefore, remain unchanged whether operating on gasoline or a blend. Fuel consumption is increased, however, in proportion to the oxygen content of the blends. In this respect richly calibrated open-loop systems may appear to have an advantage with oxygenated blends compared to closed-loop systems because they have a potential for increased fuel economy in terms of energy, miles per Btu. However, this characteristic would be difficult to perceive and is of questionable appeal to a consumer who is used to the concept of miles per gallon.

OVERVIEW OF VOLATILITY AND VEHICLE RESPONSE

Gasoline-oxygenate blends exhibit volatility characteristics unlike those of gasoline. Adjustment of hydrocarbon components to accommodate oxygenates and maintain traditional volatility limits does not always

result in vehicle performance as predicted by correlations developed with gasolines. Vehicle testing is costly and time-consuming but has been found to be the only way to determine the performance of gasoline containing non-hydrocarbon components.

The EPA is primarily concerned with fuel properties as they affect vehicle evaporative and exhaust emissions and refueling losses. Another factor of great interest is driveability (cold, warm, and hot) as it affects customer acceptance and potential tampering and misfueling.

Among the oxygenates the alcohols (but not ethers) require the application of more heat for vaporization than the gasoline components they replace (see Table 1). The need for heat becomes more critical if heavier hydrocarbons are utilized to restore distillation characteristics to meet ASTM gasoline standards. Driveability at low and intermediate temperatures can be adversely affected by blends of this type. Low carbon number alcohols also elevate volatility of the blend by increasing vapor pressure and reducing the temperature at which the middle portion evaporates. Ethers, unlike alcohols, do not significantly affect vapor pressure but do depress the middle portion of the boiling range.

The premature vaporization of blend components within the fuel system of a vehicle can result in vapor lock—sporadic or incomplete fuel delivery to the point of final discharge to the inlet manifold or cylinder intake port. Closed-loop fuel controls do not eliminate fuel-related vapor lock problems. However, submerged, in-tank fuel pumps provide much more resistance to vapor lock than did the engine-mounted pumps formerly in common use. Fuel injection systems with the supply pump at the fuel tank can deliver fuel to the injector at pressures as high as 55 pounds per square inch gauge (psig) and provide much greater tolerance of volatile fuels than is attainable with carbureted systems.

Standardized laboratory tests for vapor pressure and vapor-to-liquid ratio are unsuitable for gasoline-alcohol blends because the procedures expose the blend to substances that have an affinity for alcohol. The standard RVP test (ASTM D 323) is performed by a method that allows contact with water. However, with blends the method must be modified to prevent contact of the sample chamber with moisture. Likewise, the sealant and heat transfer medium for the vapor-liquid ratio test (ASTM D 2533), which is conventionally glycerin, could extract alcohol from the blend and bias test results. Replacing the glycerin with mercury is one way to determine the vapor-to-liquid ratio of gasoline-alcohol blends.

PERCEPTION OF VEHICLE PERFORMANCE

Several vehicle operating characteristics that are influenced by fuel parameters are detectable by a driver to varying degrees. These characteristics include driveability, combustion knock, and fuel economy.

Driveability: Low Temperature Starting

In order to start a cold engine, a sufficient amount of the fuel charge must be present in vapor form in the engine cylinders to initiate and sustain combustion. Generally, for gasolines, increased RVP and lower front-end distillation temperature improve cold starting performance. However, gasoline-alcohol blends behave differently and can exhibit volatility characteristics at low temperature that impair starting. Analytical test methods traditionally used to measure properties that correlate with low temperature starting characteristics, RVP and ASTM D 86 distillation, are performed at elevated temperatures. Blend volatility characteristics at low temperatures may not correlate with the RVP and distillation test results in the same way as for gasoline. New correlations may need to be developed for blends.

Blends of alcohols and hydrocarbons form non-ideal solutions. The portion of vapor represented by the alcohol is much larger than would be expected, either from the concentration of alcohol in the blend or its vapor pressure. As a result of this non-ideal behavior the vapor pressure generated by the combination of an alcohol and a hydrocarbon is greater than the vapor pressure of either component.

Another factor related to cold starting is the heat required to vaporize a blend. Alcohol, but not ether, blends will always require more heat to vaporize than a typical gasoline. For example, a blend containing 5 percent methanol needs 14 percent more heat to vaporize completely than does gasoline. To determine the engine response to this factor, engine tests were conducted at temperatures from 60°F to –40°F, and the mixture richness required for starting was measured.[72] The starting performance of gasoline with 8.9 psi RVP was compared with that of a blend with 11.6 psi RVP and composed of the same gasoline splash-blended with 10 percent by volume methanol. The starting performance was not improved with the high vapor pressure blend and, at stoichiometric mixture ratios for each fuel, gasoline allowed engine starting at 41°F whereas the blend would not allow starting below 59°F. A 10 percent methanol blend also was made by removing volatile fractions from the base gasoline to match the 8.9 psi RVP gasoline. With this blend starting performance was substantially poorer — the engine would not start at tempera-

tures below 59°F unless the mixture strength was enriched about 100 percent above the stoichiometric fuelair ratio of the blend. At very low temperature, -22°F, gasoline started the engine with a mixture eight times richer than stoichiometry, but the blend with matched RVP required a mixture strength of fourteen times richer than stoichiometry. It should be noted that cold engines are always started with a mixture richer than stoichiometric to supply a combustible vapor-air mixture to the cylinders. Therefore, these experiments only demonstrate relative difficulties in starting characteristics, not whether an engine will start when using a blend. The relative difficulties largely depend on the model year of the vehicle. With the wide spectrum of cars on the road today the relative difficulties in starting during these experiments can be related to the number of vehicles that may experience starting difficulties in cold weather.

Other concerns about low temperature fuel delivery characteristics of blends are a) increased viscosity of blends such as gasohol that may impede fuel flow within carburetors and b) water separation due to reduced solubility at low temperatures resulting in a free water/alcohol phase in the vehicle fuel system. Phase separation at low temperatures with methanol is less of a problem with high aromatics content gasolines and can be greatly minimized by the use of cosolvents. Vehicles may not start or operate on a separated blend.[71]

Driveability: Moderate Temperatures

Less forgivable to drivers than starting problems at extremely low temperatures are operating peculiarities during startup and drive-away at moderate temperatures. Through decades of cooperative research the automobile and oil industries have evaluated vehicle driveability from the viewpoint of the driver and have developed rating methods that quantify driveability.

Factors that contribute to a good driveability rating include quick starting, stall-free engine warmup, smooth idle, hesitation-free response to throttle opening, surge-free operation under cruise conditions, and freedom from vapor lock. Driveability commonly is rated at idle, during acceleration, and under cruise conditions as the car is driven through a prescribed cycle. The cycle is repeated several times, and demerits are assigned for substandard operation in any phase of the cycle. The final driveability rating becomes a composite of all of the assigned demerits. The engine starting time and the number of stalls witnessed during the test cycle are measured readily and objectively. Stalls during maneuvers are regarded as major defects and are assigned 32 demerits each.

Weighted demerits are calculated from driveability malfunctions detected during the test cycle by the drivers. For example, if "surge" was observed, its weighting factor of 4 would be multiplied by the severity of the surge (for example, trace = 1, moderate = 2, and heavy = 4) to give the weighted demerit for that event. An ideal combination of vehicle and fuel will normally have few demerits, but a badly matched combination can be assigned several hundred demerits or more.

Before emissions controls engines had simple fuel metering systems set to run slightly rich to provide excellent, dependable driveability, particularly during warmup. When set to run lean, an engine is prone to exhibit driveability defects. Such problems were apparent in the 1973/1974 models, which were generally set lean to reduce exhaust emissions of HC and CO and incorporated relatively unsophisticated systems of exhaust-gas recirculation for control of NO_x. Owners complained of stalling, hesitation, and surging. The introduction of the exhaust oxidation catalyst with the 1975 models permitted a return to richer calibrations and the dependable driveability of cars prior to emissions controls.

A number of extensive road test programs have been conducted by several organizations to assess the influence of oxygenated blends on the driveability of vehicles that embodied various technologies. Several driveability programs, conducted at ambient temperatures ranging from 30°F to 83°F, are summarized in Table 13 to illustrate the effects of gasoline-alcohol blends.[71, 73-77] Coordinating Research Council (CRC) procedures were followed for measuring driveability, and results are reported in terms of total driveability demerits weighted in accordance with the system described previously.

In three of the test programs listed in Table 13, both vehicles with open-loop fuel control systems and vehicles with closed-loop fuel control systems had poorer driveability when gasoline-alcohol blends were used.[73, 74, 77] Alcohols in gasolines increased driveability demerits an average of 23 demerits in vehicles with open-loop controls and increased an average of 26 demerits in vehicles with closed-loop fuel controls. Matching volatility characteristics such as RVP, $T_{V/L=20}$, or distillation did not eliminate driveability deterioration attributable to alcohols in all vehicle groups.

ARCO reported results of a large field test of driveability using gasoline, gasohol, blends containing 4.5 percent by volume methanol with 4.5 percent by volume GTBA as cosolvent, and blends containing 16 percent by volume GTBA. The fleet test consisted of 150

Table 13—Summary — Driveability Tests — Moderate Temperatures

Reference	Ambient Temperature and Test Procedure	Models	Fuel Control Loop Open	Fuel Control Loop Closed	Composition	RVP, psi	Evap. Temp. °F 10%	Evap. Temp. °F 50%	Evap. Temp. °F 90%	Driveability Demerits (Average Total Weighted)
71	30–81°F[a]; road test; CRC 1972 intermediate temperature procedure CRC #483 (March '76)	1966–74 Models: GMC	14	—	Base gasoline	10.4	118	216	313	66
					Base + 10 volume percent methanol	12.9	111	232	315	135
73	50–70°F; road test; CRC 1977 intermediate temperature procedure CRC #499 (Sept '78)	1980 Models: GMC, Ford, Chrysler	7	—	Base gasoline	9.6	116	220	325	Open-loop 22 / Closed-loop 34
					Base + 10.0 volume percent ethanol (splash-blend)	10.5	124	198	318	Open-loop 34 / Closed-loop 45
		1980 Models: GMC, Ford, Chrysler, Volvo	—	7	Base + 9.7 volume percent ethanol (matched RVP)	9.4	134	216	324	Open-loop 50 / Closed-loop 59
					Base + 9.8 volume percent ethanol (matched RVP and distillation)	9.4	130	220	324	Open-loop 34 / Closed-loop 54
74[b]	50–70°F; road tests; CRC 1977 intermediate temperature procedure CRC #499 (Sept '78)	1980 Models: GMC, Ford, Chrysler	5	5	Base gasoline	9.2	124	224	318	Open-loop 47 / Closed-loop 54
					Base + 9.6 volume percent methanol (matched RVP and distillation)	8.6	123	223	322	Open-loop 133 / Closed-loop 107
					Base + 2.6 volume percent methanol (matched RVP and distillation)	8.5	120	232	337	Open-loop 77 / Closed-loop 78
					Base + 3.4 volume percent methanol + 1.2 volume percent isobutyl alcohol (matched RVP and distillation)	8.1	124	225	324	Open-loop 83 / Closed-loop 84

Table 13—Continued

Reference	Ambient Temperature and Test Procedure	Vehicle Description Models	Fuel Control Loop Open	Fuel Control Loop Closed	Test Fuels Composition	RVP, psi	Evaporated Temperature, °F 10%	50%	90%	Driveability Demerits, (Average Total Weighted)
75	46–63°F; road tests; CRC 1977 intermediate temperature procedure CRC #499 (Sept '78)	1980–81 Models: GMC	—	2	Gasoline (Indolene)	9.0	129	225	318	26
					Indolene + 6.7 volume percent methanol + 3.3 volume percent butyl alcohol	10.3	122	221	309	79
76[c]	38–65°F; road tests; CRC 1977 intermediate temperature procedure CRC #499 (Sept '78)	1983–84 Models: GMC, Ford, Chrysler, AMC, Datsun	3	10	Base gasoline	9.7	124	256	341	All cars 71
		(Plus three cars with unidentified fuel control systems)			Base + nominal 4.5 volume percent methanol + 4.5 volume percent GTBA	11.7	117	246	336	All cars 70
					Base + nominal 4.5 volume percent methanol + 4.5 volume percent GTBA with matched RVP	9.5	124	247	337	All cars 87
					Base + nominal 4.5 volume percent methanol + 4.5 volume percent GTBA with matched distillation	10.5	120	247	333	All cars 69
					Base + 10 volume percent ethanol	11.0	121	250	339	All cars 66
77[b, c]	40–60°F; road tests; CRC 1977 intermediate temperature procedure CRC #499 (Sept '78) (modified with 127 additional cycles analyzed separately)	1979–84 Models: GMC, Ford, Chrysler	5	7	Base gasoline	8.6	135	249	341	Open-loop 55 / Closed-loop 65
					Base + 6.4 volume percent methanol with matched RVP	8.8	125	249	338	Open-loop 82 / Closed-loop 90
					Base + 8.8 volume percent ethanol with matched RVP	9.1	134	243	338	Open-loop 66 / Closed-loop 79

Table 13—Continued

Reference	Ambient Temperature and Test Procedure	Vehicle Description			Test Fuels					Driveability Demerits, (Average Total Weighted)	
		Models	Fuel Control Loop Open	Closed	Composition	RVP, psi	Evaporated Temperature, °F 10%	50%	90%		
77 [b, c]	40–60°F; road tests; CRC 1977 intermediate temperature procedure CRC #499 (Sept '78) (modified with 127 additional cycles analyzed separately) (Continued)	1979–84 Models: GMC, Ford, Chrysler, Toyota	5	7	Base gasoline	8.6	135	249	341	Open-loop Closed-loop	95 59
					Base + 4.8 volume percent methanol + 4.9 volume percent GTBA with matched RVP	8.8	128	242	339	Open-loop Closed-loop	104 105
		1979–84 Models: GMC, Ford, Chrysler, Nissan	5	7	Base gasoline	8.6	135	249	341	Open-loop Closed-loop	64 57
					Base + 4.8 volume percent methanol + 4.9 volume percent GTBA with matched RVP	8.8	128	242	339	Open-loop Closed-loop	117 92
					Base + 4.4 volume percent methanol + 3.5 volume percent ethanol with matched RVP	8.9	128	246	340	Open-loop Closed-loop	120 91

Notes:
[a] Maximum temperature difference between each comparison was less than 18°F.
[b] Data on other gasoline-oxygenate blends are reported in this reference but not cited here.
[c] Other data on blend effects on performance with higher RVP gasolines are available from this program.

employee-owned cars in which driveability problems of the cars were reported as the vehicles were operated on gasoline and the blends throughout the summer and winter seasons.[78] Drivers logged daily observations of driveability, including any difficulties encountered such as hard starts, rough idle, stalls, and hesitation or stumble. Base gasoline volatility varied seasonally, as typical for the test area, and the fuels were made by splash-blending the alcohol mixtures with base gasoline. Volatility of the blends was not controlled, and the RVP of the gasoline-methanol/GTBA blend, for example, was as much as 2.3 psi higher than that of the base gasoline.

The results from these evaluations are summarized in Figure 20. Base gasolines were at least 98 percent problem-free during both seasons. Among the blends tested, gasohol was closest to gasoline in the frequency of reported problems. For the gasoline-methanol/ GTBA blends, which generally had the least problem-free performance, the drivers had 90 percent problem-free operation with a cold engine in the summer and 96 percent problem-free operation in the winter. It was concluded that the driveability performance of all the blends would be equally acceptable to the consumer as that for gasohol. However, the RVP of the methanol blends were not controlled and did not conform to EPA waiver requirements.

Amoco conducted a blind survey of driver reactions to driveability effects of seasonal blends containing 5 percent by volume methanol and 5 percent by volume GTBA. These blends met the limits of ASTM D 439 volatility classes C, D, and E.[33,79] The same drivers evaluated gasolines of the same classes in the experiment. Driver satisfaction with car performance increased with the use of more volatile gasolines and also increased at higher ambient operating temperatures. But as shown in Figure 21, drivers were consistently less satisfied with the blends than they were with gasolines of equivalent volatility.

General Motors Research (GMR) demonstrated in a 1973 model car that driveability with gasoline-alcohol blends deteriorates as the mixture strength becomes leaner.[71] Figure 22 shows that similar driveability demerits were incurred when the mixture strength was made lean. This can be accomplished either by alcohol addition or by mechanical adjustment of the carburetor. The increase in volatility of blends due to alcohol addition, as indicated by standard RVP and distillation tests, would predict a driveability bonus based on cor-
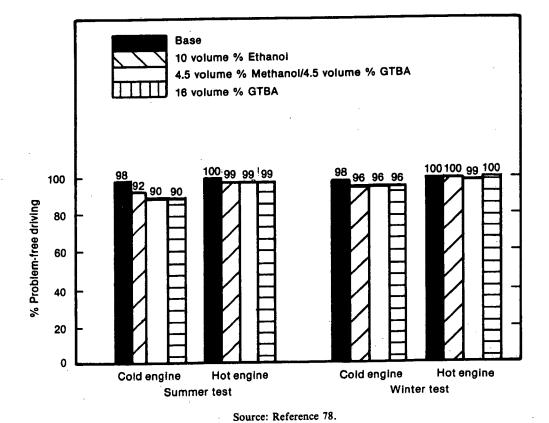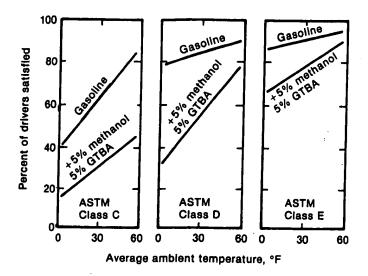

Source: Reference 78.

Figure 20—Fleet Test Driveability Results

Source: Reference 79.

Figure 21—Results of Customer Driveability Survey

relations developed for gasolines. However, increased volatility due to alcohol blending did not influence driveability at these moderate temperatures as witnessed by the single curve in the figure.

Driveability experienced with gasohol blends in fleets has been found to be generally poorer in subjective comparison with gasoline over long time frames. A large study summarized the performance of gasohol in three fleets totaling 108 vehicles from model years 1974 to 1981.[80] Gasohol complaints were statistically higher than gasoline complaints with respect to starting, stalls, rough idle, hesitation, and loss of power. Thus, reports of driveability problems with gasohol in user service confirm the performance deterioration observed in controlled testing.

At equal concentrations the higher carbon number alcohols and ethers, due to their lower latent heat of vaporization, do not seem to influence driveability at moderate temperatures as severely as methanol and ethanol. The effects of butyl alcohols and ethers on volatility properties of blends are also less pronounced, as discussed in Chapter 2, although only the ethers are similar to gasoline with respect to latent heat of vaporization. At equal volumetric concentrations the effects of oxygenates on gasoline properties are diminished as the properties of the oxygenates approach those of the hydrocarbons they replace. MTBE is a good example of such a material because its similarities to hydrocarbons allow it to be easily accommodated as a gasoline component. Distortion of the distillation curve with MTBE,

although significant at similar oxygen content, is minor when compared to the effects of allowable concentrations of methanol or ethanol. MTBE with a blending RVP of about 9 psi does not significantly increase the vapor pressure of most gasolines but is more likely to result in a blend with a slightly reduced RVP. Because the stoichiometry of MTBE more closely resembles that of gasoline, its enleanment effects are not as serious as those observed with methanol and ethanol at allowable levels. Thus, it is not surprising that the automobile manufacturers consider MTBE blends as being equivalent to gasoline.[35, 81]

Hot Weather Driveability and Vapor Lock

The primary fuel-related concern that occurs at elevated ambient temperatures is vapor lock. Vapor lock is caused by premature vaporization of fuel, impeding subsequent fuel supply to the cylinders. Oxygenated blends, particularly those with methanol or
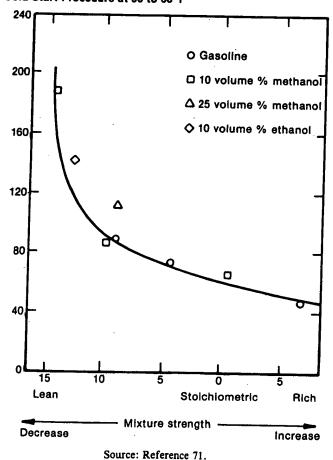

Source: Reference 71.

Figure 22—Effect of Fuel-Air Mixture Strength on Driveability at Moderate Temperatures

ethanol, have unusual volatility characteristics that are not accurately characterized using the test methods developed for gasolines.

The vapor-forming tendencies of gasolines in vehicle fuel systems have traditionally been described by $T_{V/L=20}$. A gasoline with a high volatility has a low $T_{V/L=20}$. Because of the factors discussed in Chapter 2, calculations for $T_{V/L=20}$, such as the ASTM D 439 linear equation, which uses RVP and distillation data, will not predict measured $T_{V/L=20}$ or vehicle performance for oxygenated blends. The effects are particularly pronounced for lower RVP gasolines.

The effects of gasoline volatility on vehicle driveability and performance at elevated ambient temperatures can be measured using techniques that use a demerit system similar to the system used for driveability at moderate temperatures. Historically, however, the effect of fuel volatility on vehicle performance at high temperatures has been measured in terms of the reduced accelerating capability. The formation and transport of vapors within the fuel system can reduce liquid fuel delivery under conditions of high demand such as full power. The term vapor lock has been used to describe the phenomenon and is measured by the increase in time to accelerate from low to high speed.

Table 14 summarizes the results of three test programs that measured the effects of gasoline-alcohol blends on vehicle performance at ambient temperatures between 80°F and 100°F.[73, 74, 82] In the 1980 CRC program, at 100°F, splash-blended gasohol increased acceleration time by 26 percent in open-loop vehicles but had insignificant effect on closed-loop vehicles. With a 9.7 percent by volume ethanol blend adjusted to match the RVP of the base gasoline, there was no significant difference in vapor lock performance. In another CRC test of the effects of gasoline-methanol blends with matched RVP and distillation no vapor lock occurred, even with a blend containing 9.6 percent by volume methanol.

Another CRC program, not listed in Table 14, tested the vapor lock response of fourteen 1984 model passenger cars to blends containing methanol and methanol/GTBA (4:1 and 1:1 volume ratios) at 3.5 weight percent oxygen levels.[83] The test fuels had vapor pressures as high as 18.5 RVP and $T_{V/L=20}$ as low as 92°F. The gasoline-alcohol blends performed as well as gasoline of the same $T_{V/L=20}$. At a nominal ambient temperature of 95°F equal vapor lock performance on alcohol blends was obtained at about 2 psi lower RVP. Five of the six fuel-injected vehicles in the program were insensitive to volatility and experienced no vapor lock with any of the fuels.

GMR compared the high temperature (80-90°F) driveability and vapor lock performance of methanol blends using six cars with closed-loop fuel control systems: three cars with carburetors, two with throttle-body injection, and one with port fuel injection.[82] Four blends were tested: 3 percent by volume methanol, 7 percent by volume methanol, 4.75 percent by volume methanol with 4.75 percent by volume GTBA, and 8.2 percent by volume methanol with 2.7 percent by volume GTBA. The blends were matched with two gasolines meeting ASTM specifications for volatility classes C and D, which are fuels designed for typical summer and transitional seasons in the Midwest and Northeastern U.S., respectively. Driveability demerits were greatest for two of the carbureted cars when the alcohol blends were used. The fuel injected cars and, surprisingly, one of the carbureted vehicles, performed similarly on the blends and with the gasolines. The poorer performance of the two carbureted cars, even though they had closed-loop control, was expected with the alcohol blends. As previously described, carburetors operate at very low pressure differentials and are unable to compensate for volume effects of partially vaporized fuel.

In the GMR matched-volatility vapor lock tests the carbureted vehicles also performed poorly on the blends containing the highest methanol concentrations. The performance of the fuel-injected cars was unaffected by these blends. Measurements of $T_{V/L}$ were not made for the test fuels in this program, and attempted correlations of vehicle performance with RVP and fuel type were not significant.

Toyota studied hot weather driveability and vapor lock in one car equipped with port fuel injection.[84] They found that blends containing 2.5 and 5 percent by volume methanol with GTBA or IPA as cosolvents significantly deteriorated hot starting ability after hot soak. The cause of the problem was identified as vapor lock in the fuel delivery pipe and in the injectors. The combination of decreased fuel pressure during engine cranking and boiling of fuel in the injectors caused inadequate delivery of fuel charge to start the engine. The photographs in Figure 23 show the fuel starvation encountered with the blend containing 5 percent by volume methanol and 5 percent by volume GTBA. Toyota was able to correlate hot starting with vapor pressure and distillation data only after including a methanol concentration factor.

Some European test programs found the front-end distillation characteristics to be strongly associated with hot weather performance.[85, 86] However, the correlations that were attempted most commonly employed

Table 14—Summary — Driveability Tests — High Temperatures

Reference	Ambient Temperature and Test Procedure	Vehicle Description — Fuel Control Loop			Test Fuels				Evaporated Temperature, °F			Vapor Lock, Percent Increase in Acceleration Time
		Models	Open	Closed	Composition	RVP, psi	$T_{V/L=20}$ °Fa	% Evap. @158°F	10%	50%	90%	
73	100°F; chassis dynamometer; procedure based on CRC road test procedure (1966) CRC #420 (Nov 1968)	1980 Models: GM, Ford, Chrysler	7	—	Base gasoline	9.6	136	29	116	220	325	Open-loop 3 / Closed-loop 0
					Base + 10.0 volume percent ethanol	10.5	122	40	124	198	318	Open-loop 26 / Closed-loop 8
		1980 Models: GM, Ford, Chrysler, Volvo	—	7	Base + 9.7 volume percent ethanol with matched RVP	9.4	132	35	134	216	324	Open-loop 13 / Closed-loop 9
					Base + 9.8 volume percent ethanol with matched RVP and distillation	9.4	126	32	130	220	324	Open-loop 9 / Closed-loop 10
74[b]	100°F; chassis dynamometer; (procedure same as above)	1980 Models: GM, Ford, Chrysler	5	5	Base gasoline	9.2	135	24	124	224	318	No vapor lock
					Base + 9.6 volume percent methanol with matched RVP and distillation	8.6	124	35	123	223	322	No vapor lock
					Base + 2.6 volume percent methanol with matched RVP and distillation	8.5	128	22	120	232	337	No vapor lock
					Base + 3.4 volume percent methanol + 1.2 volume percent isobutyl alcohol with matched RVP and distillation	8.1	130	23	124	225	324	No vapor lock
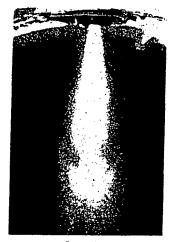
Table 14—Continued

Reference	Ambient Temperature and Test Procedure	Vehicle Description			Test Fuels							Driveability Demerits (Average Total) Weighted	
		Models	Fuel Control Loop		Composition	RVP, psi	$T_{V/L=20}$ °F[a]	% Evap. @158°F	Evaporated Temperature, °F				
			Open	Closed					10%	50%	90%		
82[b]	80-90°F; road tests; modified CRC procedure for high temperature driveability; CRC #455 (June '73)	1983 Models: GMC	—	6	Base gasoline	11.5	—	—	124	226	338	Carbureted Fuel-injected	34 27
					Base + 4.8 volume percent methanol + 4.8 volume percent GTBA with matched RVP	11.9	—	—	118	219	333	Carbureted Fuel-injected	27 35
					Base + 8.2 volume percent methanol + 2.7 volume percent GTBA with matched RVP	11.4	—	—	122	221	329	Carbureted Fuel-injected	64 24
					Base + 3.0 volume percent methanol with) matched RVP	11.6	—	—	122	228	336	Carbureted Fuel-injected	42 24
					Base + 7.0 volume percent methanol with matched RVP	11.7	—	—	122	226	334	Carbureted Fuel-injected	50 29

Notes:
[a] By modified ASTM D 2533.
[b] Data on other blends are reported in this reference.

Blend
5 volume % methanol/
5 volume % GTBA

Gasoline

Notes:
1. Fuel pressure: 49 pounds per square inch, fuel temperature: 221°F.
2. Source: Reference 84.

Figure 23—Injected Fuel Spray Pattern at High Fuel Temperature

fuel property data obtained from RVP and distillation tests, which are suitable for gasoline but may be of questionable validity for blends containing alcohols.

Currently, measured $T_{V/L=20}$ appears to be the best indicator of hot weather driveability and vapor lock tendency. Because both splash-blended ethanol and RVP adjusted methanol or methanol-cosolvent blends cause a decrease in $T_{V/L=20}$, available data suggest these blends will tend to increase the incidence of vapor lock.[83] The wide variety of existing fuel system types, and their diverse responses to blends, suggests that additional research would be appropriate to establish the most meaningful predictors of blend performance at high operating temperatures.

Full Power and Hill Climbing

Power and hill climbing ability are directly related to the heat released during combustion. As illustrated in Figure 18, the best performance is obtained with a mixture strength richer than stoichiometric. Both open-loop and closed-loop fuel control systems have calibrations set to provide close to maximum power at wide open throttle using gasoline. Blends containing oxygenates can reduce the maximum power potential because of mixture enleanment as shown in Figure 18. In pre-emission control vehicles the mixture strength for maximum power generally is set as much as 15 to 20 percent

richer than stoichiometric. Alcohol or ether blends within the range of concentration allowed by the EPA have negligible effects on full power. Some vehicles with rich calibrations may experience slightly improved acceleration performance at wide open throttle with blends due to a small increase in volumetric efficiency. Acceleration might also be improved by increased mixture charge density resulting from increased intake charge cooling due to the higher heat of vaporization of alcohols.
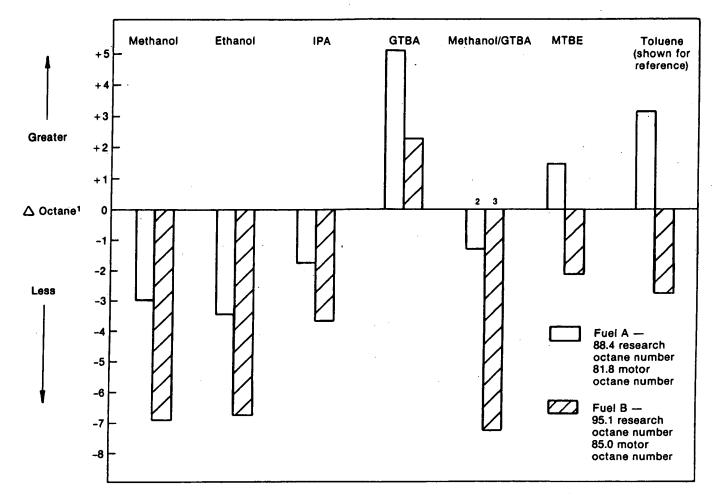
Cars calibrated for optimum fuel economy generally have fuel settings for maximum power closer to stoichiometric. Enleanment of 3 to 4 percent, typical of that caused by blends, could reduce the power of such vehicles by as much as 1 percent. In contrast, enleanment due to blends at light throttle, where mixtures are leaner, especially in the case of open-loop systems, can have observable detrimental effects on driveability.

In the survey of gasohol performance using the three fleets with 108 vehicles reported earlier, drivers of gasoline vehicles registered a 1 percent frequency of "loss of power" complaints, and drivers of gasohol vehicles reported a 2.5 percent complaint level.[80] The conditions of driving that prompted the complaints were not reported.

Antiknock Performance

The major attraction of oxygenates to the refiner is their octane blending value. Each volume percent of an oxygenate added to a typical unleaded gasoline with 87 (R+M)/2 octane increases blend octane between 0.1 and 0.3 numbers.[13] The incremental gains decrease as gasoline composition changes and the octane increases.[87] Methanol and ethanol are about equal as octane boosters and offer the highest blending octane values of the EPA-allowed oxygenates. Due to the concentration limits established by law, the largest increases in octane are obtainable with 10 percent by volume ethanol or with 11 percent by volume MTBE.

The octane blending values of oxygenates measured in cars on the road, known as Road blending values, can be considerably different than the (R+M)/2 values calculated from the ratings determined in laboratory single-cylinder knock test engines. Figure 24 shows the relation between Road blending values and (R+M)/2 blending values as determined from a CRC program that included 38 cars and two unleaded base gasolines, a premium and a regular grade.[87] Oxygenates have higher blending octane values in low octane base fuels than in the premium base fuels. Also, as shown in Figure 24, the correlation between blending values for (R+M)/2 and

Notes:
1. △Octane = Road octane blending value minus (R + M)/2 octane
    blending value. Average of two oxygenate concentrations, except
    as noted.
2. 4.4 volume percent methanol/4.4 volume percent GTBA.
3. 4.8 volume percent methanol/4.9 volume percent GTBA.
4. Source: Reference 87.

Figure 24—Effects of Oxygenates on Road Octane Performance

Road was best for the regular grade fuel. MTBE and GTBA often exhibit Road blending values better than their (R + M)/2 values in lower octane gasolines. The CRC test procedure compared octane performance at engine speeds below 3500 revolutions per minute (rpm).

As with most gasolines, oxygenated blends tend to have less knocking resistance at higher engine speeds. These effects are more pronounced with some oxygenates. Figure 25 illustrates reduced octane effectiveness of methanol blends at higher engine speeds up to 4000 rpm.[71] Figure 26 illustrates that MTBE blends may not show this effect.[81]

Based on data with methanol, some oxygenated blends may be more sensitive to the severity of engine operating conditions as defined by the greater difference between the Research and Motor Method octane numbers compared to gasoline. The increase in severity of engine operating conditions due to mixture enleanment when oxygenated blends are used is another cause of high speed knock. In effect the leaner mixture creates an operating condition more similar to the laboratory single cylinder Motor Method. Chrysler recently reported its concern about preignition damage from combustion knock with alcohol blends at very high

Source: Reference 71.
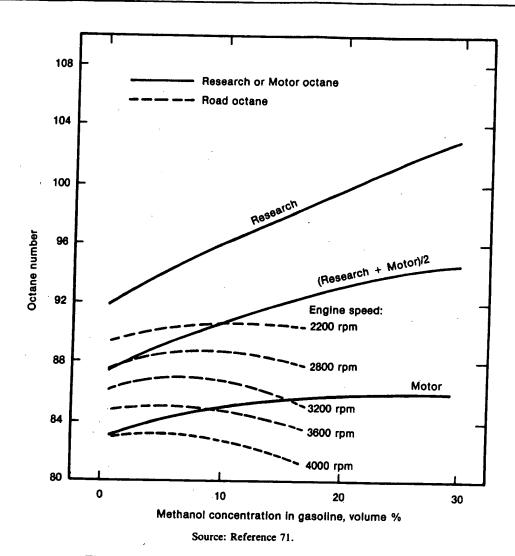
Figure 25—Effect of Methanol Concentration on
Laboratory and Road Octane Numbers

engine speeds where other vehicle noise tends to mask the audible knock.[88]

Many late model cars have been equipped with electronic knock sensors that detect combustion knock and signal computers to retard the ignition timing and reduce the knock. The occurrence of automatic ignition retardation could diminish engine power to an extent that might be recognized as a loss in performance by an observant driver.
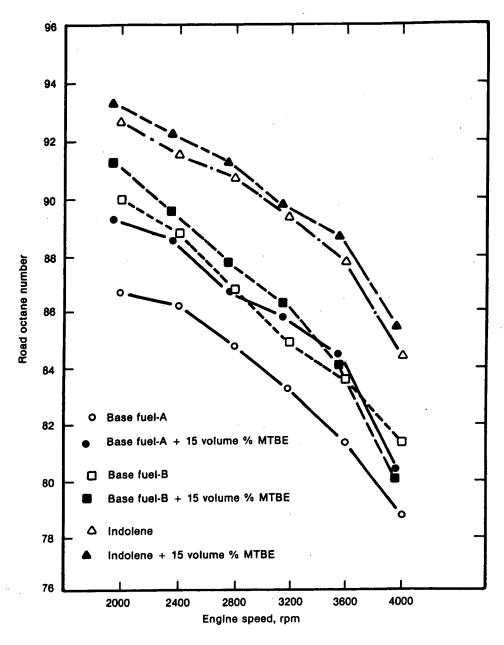
Gasohol has been known to reduce the problem of run-on, the tendency for the engine to continue to run after the ignition has been turned off. In a survey of 108 vehicles operated on gasohol a decrease in run-on, by a factor of three-to-one, was the only significant performance advantage that drivers observed gasohol to have over gasoline.[80] Blends with high alcohol concentra-

tions, such as gasohol, have superior resistance to combustion knock at low engine speed and deter run-on largely because of their higher heat requirement for vaporization.[89] Higher Research octane number (RON) gasolines also reduce run-on.

Fuel Economy

The heating value differences between currently allowable blends and gasoline, shown in Table 12, do not exceed 3.3 percent. Gasohol, with the highest oxygen content, would be expected to have the largest effect and MTBE to have the least.

A comprehensive survey of the effects of gasohol on fuel economy reported that volumetric economy was reduced 1.7 percent for a group of 256 fuel-paired vehicles ranging from model year 1973 to 1980.[3] A plot
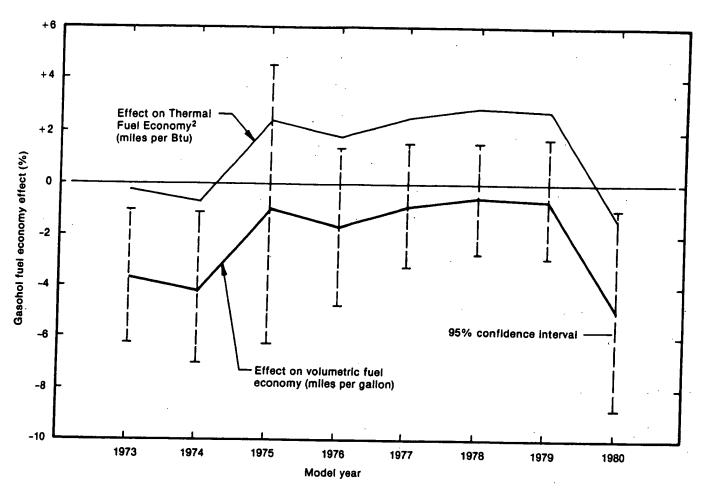
Source: Reference 81.

Figure 26— Effect of Engine Speed on Road Octane Number

of these data arranged by model year shows, in Figure 27, an apparent interaction between fuel metering technology and blend effects on fuel economy. The forty-one 1973 and 1974 model year vehicles, a group that generally employed lean mixture strengths as a means to obtain low exhaust HC and CO emissions, responded with 3.7 to 4.1 percent poorer fuel economy on gasohol. The one hundred ninety-seven 1975 to 1979 model year vehicles mostly incorporated oxidation catalyst controls as a means to meet tighter exhaust

emission limits while at the same time restoring the richer fuel-air mixtures needed to correct the driveability deficiencies of the 1973 and 1974 models. This group lost only 0.6 to 1.7 percent in fuel economy.

However, the average fuel economy loss for a group of seventeen 1980 model cars was 5.0 percent. This group included six vehicles with closed-loop fuel controls, which enable mixture adjustment and are most susceptible to reduced fuel economy when using blends.

Notes:
1. One part ethanol with nine parts gasoline.
2. Based on +3.3% for volumetric heating value difference.
3. Source: Reference 3.

Figure 27—Fuel-Paired Gasohol[1] Fuel Economy Effect Versus Vehicle Model Year

In another study twenty-three 1981 to 1983 model cars with closed-loop fuel controls experienced an average fuel economy loss of 2.3 percent using blends containing 5 percent by volume methanol and 5 percent by volume TBA.[79] In the same program six cars with open-loop controls lost 0.8 percent in fuel economy. Another group of fourteen 1982 to 1984 model cars with closed-loop controls running on gasohol in consumer service incurred 2.0 percent poorer fuel economy.[38, 79]

These observed effects coincide with the theoretical discussion of thermal fuel economy. The vehicles of 1973 and 1974 model year vintage with fixed calibrations that are set on the lean side near the point for maximum economy would be expected to experience increased fuel consumption as a result of the further enleanment due to gasohol (see Figure 18). The 1980 models experienced increased fuel consumption for an

entirely different reason; those vehicles, with their closed-loop systems, automatically compensated for the lower energy density of gasohol by metering more blend as necessary to maintain stoichiometry.

When the volumetric heating value difference of 3.3 percent between gasohol and a typical gasoline is taken into account, the fuel efficiency change in terms of heating value or energy for the 1975 to 1979 models was actually improved by 1.7 to 2.8 percent. However, the consumer does not interpret fuel economy in terms of thermal units or energy but in terms of miles per gallon or miles per dollar. And in view of the high degree of variability associated with fuel economy observations with in-use vehicles, as reflected in the wide 95 percent confidence bands of Figure 27, it is unlikely that many motorists would recognize the generally small fuel economy decreases demonstrated for gasohol. These

data were developed with gasohol; the same experience would be expected of any blend in accordance with its oxygen content.

Under a theoretical scenario that postulates a constant energy requirement for transportation regardless of fuel type, such as the closed-loop fuel control systems approach, gasohol (or any other blend of the same oxygen content) would be expected to be consumed at a rate 3.3 percent greater than that for gasoline. Thus, a car that averages 27 miles per gallon on gasoline would attain 26 miles per gallon using gasohol and would require about 15 more gallons of fuel to operate 12,000 miles on gasohol than it would need using gasoline. A typical consumer would most likely not perceive such differences among the many other in-service effects on fuel economy. Fleets, however, which consider fuel costs a major expense item, are able to document fuel consumption increases on the order of 2 percent and accordingly could analyze the cost effectiveness of using blends.

EMISSIONS EFFECTS

Vehicle emissions regulated by the EPA occur both during periods of engine operation and during vehicle shutdown. The statute sets limits for emissions of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x). The exhaust hydrocarbon contribution includes unburned components of gasoline and species generated during the combustion process. Small amounts of incompletely oxidized gasoline components, such as aldehydes, including formaldehyde, are emitted. During shutdown vehicles also emit vaporized hydrocarbons originating mostly from the more volatile fractions of the fuel.

Basic emissions characteristics are established by the design of the vehicle and the emissions control systems. But emissions can be influenced to some degree by fuel properties such as oxygen content and volatility. Even so, the technology of emissions control systems, which began with simple tuning adjustments and basic add-on devices, has developed progressively to its current state of sophistication without reliance on oxygenates.

Blends containing oxygenates directly and indirectly change the emissions characteristics of a vehicle designed for gasoline. The oxygenates approved for use in blends by EPA, as compounds of hydrogen, carbon, and oxygen, are expected to have desirable emissions features as automotive fuels.

The EPA has expressed concern in three areas in its consideration of waiver requests for the use of oxy-

genates in unleaded gasolines at various concentrations: a) increased evaporative emissions of hydrocarbons, b) increased exhaust emissions of oxides of nitrogen and aldehydes, and c) particularly in the case of methanol blends, increased exhaust emissions of formaldehyde, a suspected carcinogen.

Evaporative Emissions

Gasoline vapors can be emitted from vehicles during engine shutdown through vents in the fuel tank and carburetor and from the intake of the engine air cleaner. Since 1970 the key technology employed to control passenger car evaporative losses incorporates a charcoal-packed canister connected to vents in the fuel system. The charcoal readily adsorbs vapors of hydrocarbons and alcohols generated during vehicle shutdown and retains the adsorbed material until it can be purged with fresh air. The purged vapors are burned in the engine during vehicle operation.

The working capacity of the canister, or canisters, is established for each vehicle design by the manufacturer using certification gasoline of specified volatility. As an example of capacity, a 0.85 liter canister may have a working capacity of 30 grams and could control 97 percent of the total evaporative losses generated from a car with a 2.5 liter fuel-injected engine on the standard EPA evaporative emissions test schedule.[90] If the canister becomes saturated, any additional vapor is forced through the air-intake port of the canister into the atmosphere, a condition known as "breakthrough."

The addition of alcohols to gasoline has two effects on volatility that increase evaporative losses: a) an inordinate increase in vapor pressure, especially serious with low carbon number alcohols, and b) a depression of the distillation curve. These effects were described in Chapter 2.

Increased vapor pressure causes more vapors to be formed and driven to the charcoal canister. Oxygenate concentration in the vapor generated under hot soak from gasoline-oxygenate blends has been found to contain between 10 and 66 percent oxygenate, levels greater than the percentage of oxygenate present in the blend.[90-94] Also, vapor generated from splash blends may contain larger amounts of higher boiling point hydrocarbons than are associated with the use of gasoline.[94, 95]

Alcohol and ether vapors are adsorbed by charcoal preferentially to those of hydrocarbons.[91] Gasoline-methanol blends have been found to reduce the working capacity of a canister by 10 to 52 percent.[92] However,

the desorption characteristics of alcohols and ethers are different both from gasoline and from each other. Technical opinions of the long term effects on the working capacity of carbon canisters are not in general agreement.[91, 95, 96]
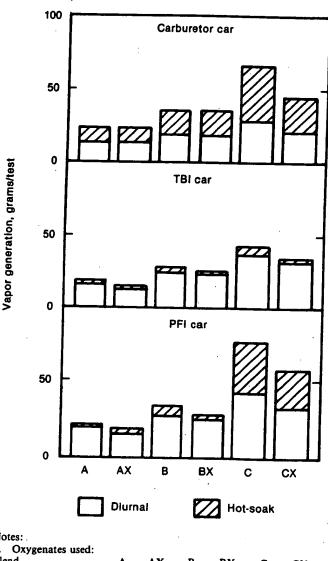
The EPA evaporative emissions test procedure includes two modes of vehicle shutdown testing during which vapor is generated: a) diurnal soak, simulating ambient daily temperature cycling, and b) hot soak, simulating shutdown following a driving cycle. The diurnal emissions originate primarily from the fuel tanks. The test procedure specifies that the fuel temperature in the tank be raised from 60°F to 84°F while evaporative emissions measurements are made. Hot soak emissions also are generated from fuel tanks, particularly, from carburetor float bowls, which can heat fuel to 150°-180°F during soak.[91] In addition, hot soak emissions can originate from port fuel injectors, which may heat fuel to above 190°F.[84]

Attempts have been made to correlate total evaporative emissions, diurnal plus hot soak, with RVP and expressions that combine RVP with ASTM D 86 distillation points. Included among those reported are a) Front End Volatility Index, previously known as the Vapor Lock Index (circa 1965) [RVP + 0.13 (percent evaporated @ 158°F)], b) Furey/King Index [RVP + 0.05 (percent evaporated @ 158°F)], and c) Evaporative Index [0.85RVP + 0.14 (percent evaporated @ 200°F) –0.32 (percent evaporated @ 100°F)]. Among these, the Evaporative Index (EI) needs some discussion, for the EPA initially granted the DuPont waiver for certain methanol/cosolvent blends with the requirement that an EI specification of the finished blends would have to be met.[97] During subsequent reconsideration of that waiver, it became obvious that EI was never intended for universal application to both gasolines and blends. After industry, through the Oxygenated Fuels Association (OFA), used the same data originally submitted by DuPont to demonstrate that there is no correlation between EI and evaporative emissions, the EPA deleted the EI requirement from the waiver in favor of following the ASTM seasonal and geographical specifications for volatility.

Work done by the CRC and many other investigators has documented that diurnal emissions increase with increased RVP, and hot soak emissions correlate well with RVP in combination with some factor of ASTM distillation.[73, 74, 78, 95] All EPA waivers except the gasohol waiver established the requirement that oxygenates could be used in blends only if the finished blend met the volatility criteria of ASTM D 439. The EPA did not

require gasohol to meet this requirement in the 1979 waiver.

GM compared the evaporative emissions of blends containing three levels of methanol/TBA with gasolines of closely matched RVP and distillation.[90] Three different fuel metering systems were tested: carburetor, TBI, and port fuel injection. As shown in Figure 28, alcohol blends generate the same vapor levels as gasolines matched to the same D 439 volatility. The reduction in emissions with fuel C when blended with alcohol

Notes:
1. Oxygenates used:

Blend	A	AX	B	BX	C	CX
Volume % methanol/ volume % TBA	0/0	4.6/4.6	0/0	6.1/5.9	0/0	5.6/5.4
RVP, psi	9.3	9.3	10.8	11.2	12.5	12.1

2. Source: Reference 90.

Figure 28—Vapor Generation With Closely-Matched Volatility Hydrocarbon and Oxygenated Fuels

was attributed to an anomaly. However, although the RVP's of the test fuels were matched at 100°F, at the test temperature of 84°F, this blend had a lower vapor pressure than the gasoline.

Exhaust Emissions

A vehicle can be expected to have different exhaust emissions characteristics when a blend is used instead of gasoline primarily because of fuel-air mixture enleanment effects. Emissions of the regulated pollutants: carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x), increase or decrease in response to mixture strength as shown in Figure 19. As previously explained, oxygenated blends will shift the operating fuel-air mixture towards the lean side of the calibrated setting.

Mixture stoichiometric effects are strongest in vehicles with open-loop fuel metering systems. For those vehicles calibrated richer than stoichiometric, usually older cars, the effect of operating on a blend will be a reduction of CO and HC, and, quite likely, a modest increase in NO_x. For non-catalyst cars of the 1973 and 1974 model years with typically lean, near stoichiometric calibrations, operation on a blend could produce a modest reduction in CO but cause sufficient mixture leanness to result in poor combustion and a consequent increase in unburned HC. Catalyst-equipped cars with open-loop systems generally show some reduction in CO and HC and small increases in NO_x. Reductions of CO and HC emissions can be observed upstream of the catalyst but are less pronounced after the exhaust passes through a functioning (warmed-up) catalyst. Changes in the emissions of NO_x, however, can be observed at the tailpipe in vehicles with open-loop systems.

The fuel-air ratio of vehicles with closed-loop fuel control is affected by blends only when operated in an open-loop mode as during warmup and full power. During open-loop modes the exhaust emissions will change in response to a lean shift from the fixed settings, similar to vehicles with open-loop systems. The net emissions change of vehicles with closed-loop systems depends upon the portion of operating time in the open-loop mode, which is typically a few minutes or less after a cold start.

Most of the exhaust emissions comparisons for blend effects employed the EPA Federal Test Procedure, which includes "cold" startup and warmup phases during which a vehicle operates mostly in an open-loop mode. Results from tests of this type may mask the effectiveness of the closed-loop system to compensate for stoichiometric differences between blends and gasolines.

A summary of the effects of oxygenated blends on the exhaust emissions of HC, CO, and NO_x developed from eleven test programs is shown in Figure 29.[71,73-75,78,91,93,97-100] From these data it is apparent that both alcohols and ethers have similar abilities to produce significant changes in exhaust emissions. Also, the response of vehicles to blends appears to be greater in vehicles of older technology.

Oxygenated blends caused leaner mixture operation as evidenced by reductions of HC and CO emissions observed at the tailpipe. Vehicles with open-loop fuel controls, typically with higher emissions than vehicles with closed-loop controls, showed larger reductions in HC and CO. The effects of blends on NO_x, however, were variable. Of the 33 data sets shown in Figure 29, 19 showed increased NO_x emissions, and the responses ranged from an increase of 0.47 grams per mile to a reduction of 0.43 grams per mile. As previously discussed, depending upon the calibration of the fuel system, blends can lean the mixture strength beyond that for the peak production of NO_x and result in reductions of those emissions.

The emissions of ethanol[73] and methanol[74] were measured in two CRC test programs and found to be 0.0065 gram ethanol/mile for the 10 percent by volume ethanol blends and 0.0157 gram methanol/mile for the 10 percent by volume methanol blend. These values represent less than 5 percent of the total exhaust organic (hydrocarbon plus oxygenated hydrocarbon) fraction. Concern about methanol emissions from vehicles designed to run on neat or near-neat methanol is increasing and will be addressed in Chapter 5.

The exhaust from vehicles operating on gasoline commonly contains a spectrum of partially oxidized HC species known as aldehydes. These compounds are not considered to contribute significantly to atmospheric pollution at current gasoline vehicle emission levels by the EPA and are not regulated. However, aldehydes are photochemically reactive and can cause eye and mucous membrane irritation. They are difficult to measure because they are easily lost in sampling systems due to chemical reactions or thermal decomposition. Acetaldehyde and formaldehyde are two of the compounds most commonly identified in the exhaust from vehicles running on gasoline. Greater amounts of aldehydes can be generated when alcohol blends are used because the partial oxidation of methanol or ethanol directly produces formaldehyde or acetaldehyde.

Tests with open-loop fuel-control vehicles — Closed-loop fuel controls — Tests with combinations of vehicles
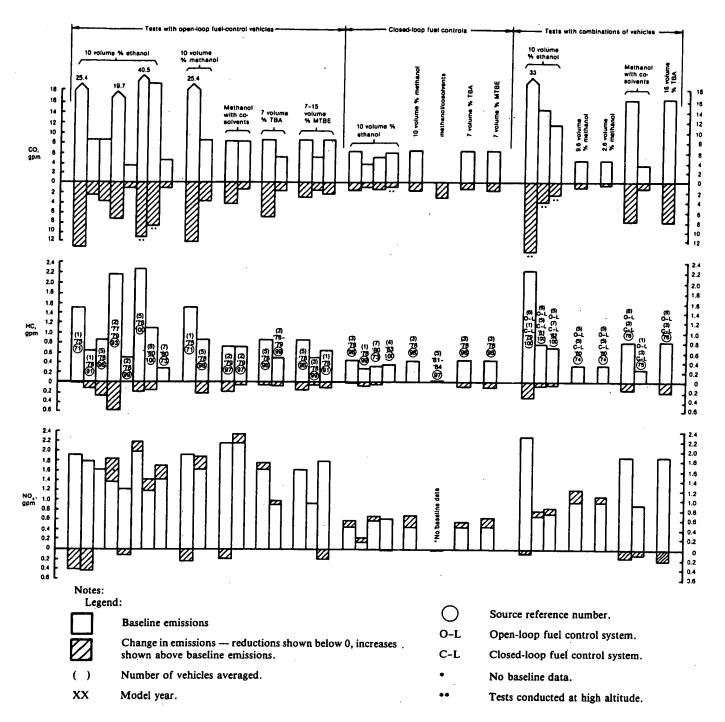
Figure 29—Effect of Oxygenates on FTP Tailpipe Emissions

Notes:
Legend:

☐   Baseline emissions

▨   Change in emissions — reductions shown below 0, increases shown above baseline emissions.

( )   Number of vehicles averaged.

XX   Model year.

○   Source reference number.

O-L   Open-loop fuel control system.

C-L   Closed-loop fuel control system.

*   No baseline data.

**   Tests conducted at high altitude.

Exhaust oxidation catalysts can remove most aldehydes, and during closed-loop operation three-way catalysts appear to be even more efficient at eliminating them. Aldehydes that survive the combustion process and the catalytic converter are present in the exhaust in very low concentrations relative to HC.[101] In the CRC tests of ethanol blends in open-loop cars tailpipe aldehyde emissions averaged 0.012 grams/mile or 50 percent higher than with gasoline. They did not increase significantly in closed-loop vehicles with three-way catalyst technology.[74] In the CRC methanol blend program no significant difference in aldehyde emissions was observed between any of the blends and gasoline.[73] It is possible that the laboratory procedure used in this

program could not accurately measure small levels of aldehydes and, thus, no difference was observed. An EPA test program utilizing two 1984 model cars found aldehyde emissions averaged 0.007 grams/mile, an increase of 49 percent over gasoline, when a blend containing 4.5 percent by volume methanol and 5.7 percent by volume TBA was used.[92] The program identified about 80 percent of the aldehyde increase, or 0.002 grams/mile, as formaldehyde emission.

Techniques to properly sample and accurately identify exhaust formaldehyde are very complex and are continuing to be developed. They will be especially needed for use in measuring emissions from vehicles operating on neat, or near-neat, methanol. More will be covered on formaldehyde emissions from these vehicles in Chapter 5.

VEHICLE RELIABILITY ASPECTS

Many of the long term effects of blends containing alcohols on materials in the vehicle fuel system and on engine durability are unknown. A wide variety of materials are in direct contact with fuel in the vehicle, and their integrity must be maintained to ensure performance that is safe and dependable and to provide satisfactory emissions control and economy. In customer service few reports of catastrophic fuel system failures attributable to blends have been authenticated. One manufacturer found blends resulted in driveability complaints caused by sticking carburetor accelerator pump cups made of elastomeric material.[102] Two other manufacturers observed gasohol to cause severe corrosion in fuel tanks and fuel lines in customer service.[103, 104]

Basic engine durability has not been reported to be affected by blends. Data show that the addition of alcohols may reduce the effectiveness of some gasoline detergent additives and corrosion inhibitors such that higher concentrations of these additives are needed to provide equivalent performance in a gasoline-alcohol blend.[26, 105] Part of the problem of poorer detergent additive performance may be that the addition of alcohol increases the amount of deposit formed in carburetor throttle bodies.[106] There are some data to show that deposits on intake valves are increased with the use of alcohol blends and cause driveability problems for at least one manufacturer's cars during warmup.[107] The problem, first observed in Germany due to the widespread use of methanol blends, was also observed in the United States and appeared to occur with blends that do not contain an adequate amount of deposit control additive.

Much of the uncertainty that the automobile manufacturers have about the use of alcohol blends is due to

potential materials incompatibility. Several manufacturers in the past have recommended that owners avoid the use of blends containing ethanol or methanol in order to protect their warranty.[64] MTBE has not caused any known fuel system problems, presumably because its chemical and physical properties are close to those of gasoline. Manufacturer concerns about alcohol blends are usually expressed in owner's manuals as references to "fuel system damage" and "damage to critical fuel system components."

Recommendations are changing as manufacturers have an opportunity to incorporate materials of known compatibility into the fuel systems of their new models. For example, GM and Volkswagen first indicated approval of the use of ethanol blends for their 1980 models. Chrysler and Ford first approved the use of ethanol blends for 1981 models and Volvo for its 1985 models. American Motors Corporation (AMC) recommended against the exclusive use of gasohol because of evidence that its fuel systems were subject to corrosion. For its 1984 models AMC said the use of blends with up to 3 percent by volume methanol with an equal volume of cosolvent and with corrosion inhibitor may be acceptable. Methanol blends currently approved by EPA were noted as acceptable for 1985 models by GM, Ford, AMC, Mercedes-Benz, BMW, and Jaguar. However, three other manufacturers indicated approval with qualifications, and ten others recommended against the use of methanol blends for their 1985 models. Most indicated that test work was still in progress.

In 1987 EPA conducted a survey of ten major automobile manufacturers regarding their attitudes toward gasoline-ethanol and gasoline-methanol blends.[68] Their survey gave the following results:

Manufacturer	Ethanol Blend	Methanol Blend
AMC	Maximum 10%[a]	Maximum 5%[a, b]
Chrysler	Maximum 10%[a]	Do not use
Ford	Maximum 10%[a]	Maximum 5%[a, b]
GM	Maximum 10%[a, c]	Maximum 5%[a, b]
Toyota	Maximum 10%[a]	Maximum 5%[b]
Nissan	Maximum 10%[a, d]	Maximum 5%[a, b, d]
Honda	Maximum 10%[a, d]	Maximum 5%[a, b, d]
Mazda	Maximum 10%[a, d]	Do not use[d]
Volkswagen	Maximum 10%[a]	Do not use
Audi	Do not use	Do not use

[a]Manufacturer recommends using gasoline should driveability problems occur.

[b]Provided the fuel contains the necessary cosolvents and corrosion inhibitors.

[c]Manufacturer makes no reference to ethanol blended fuels as "gasohol."

[d]Manufacturer refers to both ethanol and methanol blended fuels as "gasohol."

Because the chemical effects of blends on plastics, elastomers, and metals are functions of time, they often cannot be foreseen by accelerated laboratory testing. Deposits and wear change the surfaces of engine parts and, in some respects, are more readily observable than the deterioration of plastics or elastomers within the fuel system. The longest systematic vehicle tests of materials rarely exceed a 2-year period, which is a small interval in the expected life of a vehicle. A brief discussion of blend effects on vehicle durability and reliability follows.
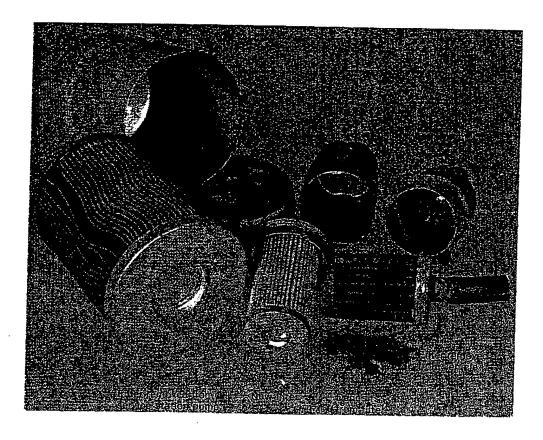
Fuel Filter Plugging

Fuel filter plugging is caused by debris in the fuel and results in fuel starvation and ultimate vehicle shutdown. In filter designs that incorporate a pressure relief valve, when the filter becomes blocked, the vehicle may continue to operate but debris may bypass the filter and be carried to the carburetor or fuel metering device. Dirt in a precision fuel metering device can cause serious problems that require expensive repairs. Older vehicles fre-

quently harbor deposits of dirt, gums, and corrosion products within the fuel tank and lines but continue to operate without any apparent problem on gasoline. Alcohol blends, however, because of their solvent nature, can loosen such residues and allow the debris to be transported downstream with the fuel. Figure 30 shows sectioned fuel filters and the trapped particulates from vehicles that were switched from gasoline to gasohol. The filters were replaced due to driver complaints but not before allowing fine sediment to enter the carburetors.[108]

Fuel filter plugging may occur several times after switching to gasoline-alcohol blends and is more troublesome in older cars simply because more dirt has accumulated in the fuel system. The Motor Vehicle Manufacturers Association (MVMA) recommends that the motorist should consider carrying a spare filter during a transition period to gasoline-alcohol blends covering several tank fills.[109]

Alcohol reduces the surface tension characteristics of Saran and similar plastic materials commonly used in

Source: Reference 108.

Figure 30—Fuel Filter Elements

fuel tank strainers or water separators. The lowered surface tension allows the passage of water that would normally be restricted in the presence of gasoline.

Blend Effects on Fuel System Plastics, Elastomers, and Metals

Many critical fuel system components in addition to the fuel tank strainer employ plastics and soft, flexible elastomers. Plastic parts are designed to have good strength and dimensional stability. Some plastic materials such as Nylon 66 are essentially impervious to gasoline but react to alcohol blends much as they do to water — by swelling and losing tensile strength.[30] Alcohol blends also have been reported to soften polyester resins and loosen fibers from the fiberglass filler.[26]

Fuel system components made from elastomers must not crack, leak, or become permeable to fuel. They must retain flexibility, strength, and optimum hardness to provide required sealing. Permeability of fuel system components and the transmission of fuel to the atmosphere may contribute significantly to vehicle evaporative losses. Materials destined for exclusive use with either 100 percent alcohols or gasoline do not have to contend with the chemical attack associated with the use of blends. A mixture of gasoline with alcohol upsets the normal hydrogen bonding of alcohol and sets loose polar groups within the blend that attack polar compounds of the plastic or elastomer.[110] Unfortunately, many polar compounds that provide elastomers with resistance to hydrocarbons are highly vulnerable to, and are displaced by, polar groups from alcohols, especially

methanol and ethanol. Fuel additives or cosolvents have generally not been found to be effective in mitigating the attack.[111] IPA, TBA, and MTBE do not seem to exhibit these solubility and polar effects on elastomers.[110] Both methanol and ethanol blends cause swelling, softening, and loss of tensile strength of elastomers such as acrylonitrile-butadiene rubber (NBR), commonly used as fuel line material with gasoline.[112-115]

Fuel lines, carburetor needle-valve tips, and accelerator pump cups made from elastomers optimized for use with gasoline have been reported to deteriorate when methanol or ethanol blends are used, especially with highly aromatic gasolines.[104, 116, 117] Elastomers selected for compatibility with alcohol blends usually perform acceptably with gasoline. Table 15 lists the swelling characteristics of several elastomers after soaking in gasoline, methanol, ethanol, MTBE, and blends containing 10 percent by volume of three oxygenates.[118] Fluorocarbon elastomers, such as Viton A, have excellent resistance to swelling in highly aromatic gasoline as well as methanol blends in the concentration range allowed by the EPA.[119] NBR performs satisfactorily with a 10 percent by volume MTBE blend but is unsatisfactory with alcohol blends or 50 percent by volume aromatics. The fluorocarbons appear to offer the best overall performance with blends and gasolines, and although costlier than most of the other materials, are being widely implemented in fuel systems of new vehicles. The older cars may be less resistive to potential elastomer problems with methanol blends, but replacement parts that are more tolerant of blends are being made available.[109]

Table 15—Comparison of the Swell of Various Elastomers in Methanol, Ethanol, and MTBE Mixtures With Gasoline

Elastomer	Volume Swell,[b] Percent, After 72-Hour Immersion in:				90% Gasoline and 10% of:		
	Gasoline[c]	Gasoline Spiked[d] to 50% Aromatics	Methanol	Ethanol	Methanol	Ethanol	MTBE
Fluorocarbon (FKM)	0	3	100	2	27	3	2
Polyester urethane	11	23	18	19	42	37	13
Fluorosilicone (FMQ)	14	16	8	6	21	18	—
Butadiene-acrylonitrile (NBR)	34	55	14	8	53	51	34
Polyacrylate (ACM)	44	120	94	101	112	136	—
Chlorosulfonated polyethylene (CSM)	49	74	1	1	41	56	48
Ethylene-propylene-diene terpolymer (EPDM)	137	143	0	13	109	124	139
Natural rubber (NR)	169	197	1	2	148	176	—

Notes:
[a]Source: Reference 118.
[b]Reference indicates that materials are considered fuel resistant if the volume swell percent is less than about 30%.
[c]Gasoline used was Indolene HO-III (30% aromatics).
[d]Spiked with toluene.

Corrosion of steel fuel tanks and pipes has been observed in long term field service with gasohol-fueled vehicles.[103, 104, 109] Extensive fuel line corrosion and tank chamber rusting occurred over a 2-year timeframe in mid-northwestern service.[103] The proper application of corrosion inhibitors appears to eliminate fuel system rusting. A major marketer of gasohol containing an effective anti-rust additive reported no evidence of corrosion in customer-service vehicles operating in Iowa.[79] Similar field experience with gasoline-methanol/TBA blends containing inhibitor has also been documented.

CHAPTER 5—NEAT AND NEAR-NEAT ALCOHOLS FOR FUELING AUTOMOTIVE VEHICLES

Alcohol Fuels for Spark-Ignition Engines

Historically, alcohols, especially methanol, have been desirable as fuels for racing engines, not only because their high octane quality allows higher engine compression ratios but because their ability to burn at very rich mixtures compared to gasoline provides important potential for internal engine cooling.[120] Racing engines are calibrated to run rich, often 40 percent richer than stoichiometric. The rich mixture, along with the lower energy content of methanol compared to gasoline, results in a methanol consumption rate about three times that of a gasoline-fueled race engine.[121] The high latent heat of vaporization of alcohols cools the cylinder, piston, combustion chambers, and mixture charge during the intake stroke. This cooling allows the incoming charge to be more dense and thus to produce more power. This is true both for naturally aspirated engines and those with pressure boosting from supercharging or turbocharging.[122] In automotive engines typical power increases of 10 percent have been observed without engine modifications using methanol as fuel instead of gasoline. Such power increases are due to increased charge density (improved volumetric efficiency).[123, 124] Further increases in power are achievable through the use of increased compression ratio.[12]

EFFECTIVE ENGINE UTILIZATION OF NEAT ALCOHOLS

To utilize alcohols most effectively, engines must be designed to take advantage of the potential for improved combustion characteristics as well as the benefits related to charge cooling. However, the thermal efficiency of engines that have not been optimized can also be improved by operation on alcohol. As discussed in Chapter 2, the lower alcohols have lower energy density compared to gasoline or diesel fuel. Because methanol contains about half the energy per gallon that a gallon of gasoline does, one might expect that miles per gallon of a methanol-powered vehicle would be half that of a similar gasoline-powered vehicle. However, improvements in efficiency due to differences between methanol and gasoline have been observed. Thermal efficiency increases of 3 to 4 percent over that obtained with gasoline have been reported.[5, 10-12] These gains in efficiency can be attributed to the following differences between the combustion characteristics of alcohol and gasoline: a) alcohols burn with lower flame temperatures and luminosity; thus, less heat is lost by conduction and radiation from the combustion chamber to the engine cooling system, b) alcohols burn faster and allow more efficient engine torque development, and c) alcohol combustion generates a larger volume of combustion products and develops higher cylinder pressures. These effects are most pronounced with methanol and decrease for higher molecular weight alcohols.

An indirect approach to vehicle fuel economy improvement entails the use of superchargers or turbochargers that allow increased engine power output similar to aircraft engine practice.[125, 126] Supercharging or turbocharging is not generally regarded as a means to increase engine thermal efficiency, but it can allow fuel economy to be improved through reduced vehicle weight made possible by the use of smaller, lighter weight engines. Note, however, that volumetric fuel economy in terms of miles per gallon will still be less for neat or near-neat alcohol fuels compared with gasoline because of the lower energy content of alcohols compared with gasoline.

A better way to improve the fuel economy of an alcohol-powered engine involves taking advantage of the superior antiknock characteristics of the alcohols. Because methanol and ethanol have high octane qualities, the compression ratio of an engine designed to run on an alcohol may be increased above that used for gasoline-powered engines. This improves both power and fuel economy, although increased friction and the poorer combustion chamber geometry at higher compression ratios may limit the improvements.[4, 120] Engine compression ratio is usually increased substantially to achieve improved performance and improved fuel economy in an alcohol-fueled engine.

Increasing compression ratio generally increases the fuel economy of gasoline-powered engines between 2 and 4 percent for each ratio number increase between 8 and 12:1.[127, 128] Higher gains in fuel economy are possible if the increased performance of the higher compression ratio engine is traded off for maximum fuel economy.[129] Alcohol-fueled engines respond comparably to compression ratio and show similar gains in fuel economy.[130, 131] Brinkman reported a 16 percent improvement in efficiency as the compression ratio was increased from 8:1 to 18:1, while maintaining optimum timing, in a methanol-fueled single cylinder engine.[12]

In Brazil the engines of about 85 to 90 percent of the new cars are designed to operate on a mixture of 95 percent ethanol and 5 percent water (referred to as 190 proof alcohol). The engines typically have compression ratios near 12:1 to utilize the high knock resistance of the fuel and deliver optimum fuel economy.[5, 132]

The thermal fuel economy benefits gained by increasing compression ratio can be traded off for reductions in exhaust emissions of alcohol-fueled engines in much the same manner as accomplished with gasoline engines. In the current methanol test program by the State of California, Ford Escorts, designed with 11.5:1 compression ratio to operate on a methanol-gasoline blend, have thermal fuel economy 16 percent better than gasoline-powered counterparts when calibrated to the same NO_x level of 1.0 grams per mile. When the methanol-gasoline cars were calibrated for a 0.4 grams per mile NO_x limit, the thermal fuel economy advantage disappeared.[133]

Further improvements in fuel economy can be achieved by taking advantage of methanol's wide flammability limits. Toyota reported improved fuel economy on the order of 10 percent with their Toyota Lean Combustion System applied to a methanol engine compared with the system at stoichiometric mixture.[134, 135]

In the United States and other countries, including West Germany and New Zealand, most of the attention directed to the use of neat alcohol fuels has been focused on methanol rather than ethanol because of manufacturing cost and supply considerations. Methanol offers the same antiknock benefits as ethanol but requires 71 percent more heat for vaporization for each unit of heat generated through combustion. This can be considered either an advantage or a disadvantage. For higher volumetric efficiency and lower mixture temperatures (as in racing), methanol would be preferable to ethanol. But for better driveability and lower emissions of unburned fuel, ethanol would be better than methanol.

DRIVEABILITY WITH NEAT OR NEAR-NEAT ALCOHOLS

Driveability experience with mass-produced alcohol-powered automobiles has been limited to Brazilian and German models that were not calibrated to meet U.S. standards for exhaust or evaporative emissions. Domestic manufacturers, however, have reported that alcohol-powered cars, after being started and warmed-up, can have the same or better driveability as gasoline cars.[5, 7, 136, 137] As for gasoline vehicles, port fuel injector fouling has occurred in some methanol vehicles and has affected driveability and emissions. New injector designs are being developed to address these problems.[138, 139]

The most important unresolved engineering problems obstructing the design and development of vehicles for use with neat alcohol are inadequate cold starting characteristics and misfiring during warmup.[140] Unsuccessful starting and misfiring during warmup result in liberal washing of cylinder walls, dilution of the engine lubricant, and cylinder bore wear.[141, 142]

Neat alcohols are insufficiently volatile to enable a cold engine to start, even at moderate temperatures. It has been reported that carburetor air temperature must be at least 109°F to enable starting with ethanol,[143] and neat methanol requires ambient temperatures above about 50 to 60°F to allow starting without extra heating or starting aids.[22, 144] Theoretically, the flammability/vapor pressure relationships for ethanol and methanol indicate that a mixture of air and excess fuel will be too lean to ignite below about 50°F.[25, 26] In an engine in which evaporative cooling and compression heating occur, actual minimum starting temperatures may differ from the theoretical temperatures.

Brazilian experience dictated the need for an onboard auxiliary supply of volatile fuel, such as a gasoline-ethanol blend, that could be introduced into the engine for cold starting. During 1981 through 1983 the California Energy Commission field tested 37 Volkswagens divided between calibrations for neat ethanol and neat methanol. All of the Volkswagens were equipped with a gasoline-assist starting system similar to that used in Brazilian production.[145] General Motors developed an onboard starting-assist system for its experimental methanol-powered light-duty vehicles, which injected propane. This system provided reliable cold starts down to -4°F.[7] Figure 31 illustrates the schematic of the GM starting system and features of other vehicle components that were modified to allow the use of neat methanol.
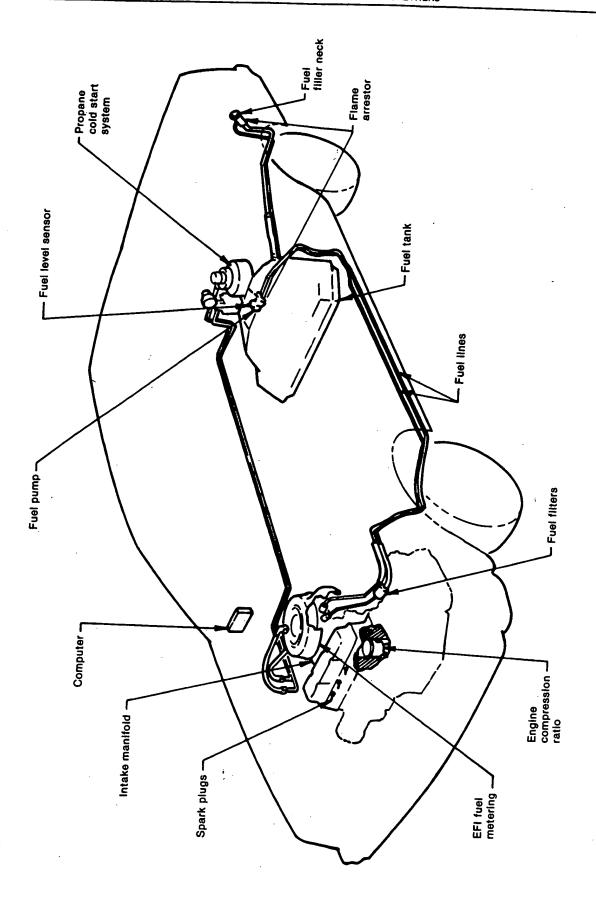
Figure 31—General Motors Methanol Vehicle Modifications

Source: Reference 7.

Propane cold start system

Fuel filler neck

Flame arrestor

Fuel level sensor

Fuel tank

Fuel pump

Fuel lines

Computer

Intake manifold

Spark plugs

Fuel filters

Engine compression ratio

EFI fuel metering

Devices have also been developed to provide increased methanol vaporization using finer atomization or auxiliary electrical heat.[8, 140] Studies have shown that methanol vaporization could be increased within the engine cylinder under cranking conditions if fuel droplets in sizes below 50 microns could be prepared. Reducing droplet size from 50 to 10 microns could lower starting temperature from 64°F to 5°F.[146] Fuel injection at the intake port appears to provide better atomization in the cylinder and in current development programs is preferred over carburetors or throttle body injection because it provides the best driveability.[7, 136, 140]

Development work with ultrasonic nozzles has demonstrated some success in achieving starting times at 41°F within 5 seconds, a reduction of 75 seconds from the time required with a carburetor.[140] However, electrical heating elements at individual cylinder intake ports have not been found very helpful as aids to cold starting with neat methanol. Starting could not be achieved at 10°F with heat application as high as 60 watts per cylinder, about 8 times the rate of heat flux needed to vaporize sufficient methanol for a lean limit flammable mixture. But this type of heating system has been adapted successfully to cars using methanol-gasoline blends as described below.[8]

Another starting method that is still under development is the use of dissociated methanol. When dissociated by heat in a burner/decomposer-heat exchanger unit, methanol becomes carbon monoxide and hydrogen gases, which can allow excellent cold starting due to the wide flammability limits of hydrogen.[140] At the present laboratory state-of-the art dissociated gases are used with atomized methanol to provide enough energy for starting and warmup.

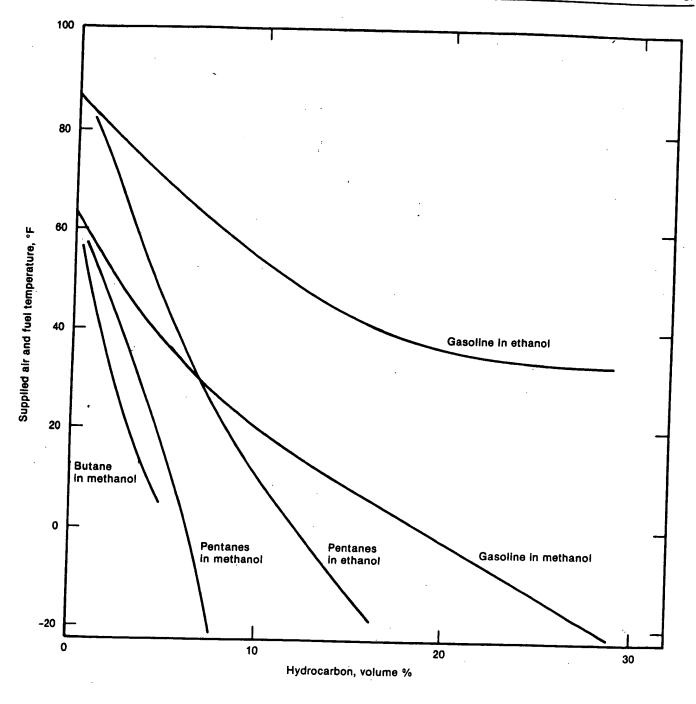## THE INCENTIVES FOR NEAR-NEAT ALCOHOL FUEL

The term "near-neat" has been coined to describe blends of methanol-hydrocarbon, or methanol-gasoline, where the primary component is alcohol. Near-neat alcohol presents the same menu of potential problems associated with gasoline-alcohol blends described in Chapter 4: vapor lock, increased evaporative emissions, and incompatibility with fuel system materials. Near-neat methanol does not afford all of the desirable emissions benefits attributed to neat methanol. Because it has little appeal as a fuel for modified compression ignition engines, there is little possibility of its use as a common fuel for both compression-ignition and spark-ignition engines.

The addition of hydrocarbons or gasoline to alcohol reduces the problem of engine cold starting with alcohol fuels. Figure 32 shows the effect of supplemental hydrocarbons and gasoline on the simulated minimum cold starting temperatures from laboratory bench tests, which allowed for evaporative cooling but not for compression heating.[25, 26] Addition of 15 percent gasoline to ethanol reduces the temperature necessary for a flammable mixture from 86°F to 45°F. Methanol responds somewhat better to addition of 15 percent gasoline, and its flammable mixture temperature was reduced from 61°F to 9°F. Ford has demonstrated engine cold start capability at temperatures as low as -20°F with the addition of 15 percent gasoline to methanol through use of computer-controlled starting systems.[4]

As shown in Figure 32, the addition of 6 percent by volume pentanes to methanol provides about the same minimum flammable temperature as the addition of 15 percent gasoline. Pentane addition to methanol was successfully used during the first two years of the State of California field test program beginning in 1980.[138] Although about 4 percent butane would do the same job as 15 percent gasoline, it would increase the vapor pressure excessively and weather quickly from the alcohol.[26] Low concentrations of dimethyl ether have also been reported to improve cold engine starting without the disadvantages of phase separation experienced with some hydrocarbons such as isopentane.[147]

Other incentives for blending gasoline into methanol relate to safety considerations. Methanol presents a special safety hazard because it burns with a flame that is invisible, particularly in daylight. Hydrocarbons blended with methanol have been found to effectively increase flame luminosity.[26] As little as 2 percent toluene, which contains 91.2 percent by weight carbon, produces high flame luminosity. However, even with 5 percent by volume toluene, the flame luminosity fades when 30 to 50 percent of the methanol remains unburned. Luminous flames can be produced by 5 percent by volume gasoline or reformate, but luminosity lasts for a shorter period and disappears, while 70 to 80 percent of the methanol still remains. A blend containing 15 percent by volume gasoline with at least 40 percent aromatics content provides a luminous flame that will persist until all of the methanol is consumed.[148]

A second concern of onboard vehicle safety is potential explosivity. Saturated vapor over neat methanol in a fuel tank is flammable at temperatures between about 45 to 110°F.[149] Ignition of methanol vapor is possible from a spark source such as the exposed brushes of an electric fuel pump in a fuel tank that has run out of fuel. GM has been experimenting with foam fillings in fuel

Source: References 25 and 26.

Figure 32—Simulated Cold Starting Minimum Temperatures Based on Laboratory Bench Tests

tanks, which essentially eliminate the continuous vapor space required for explosion hazards with flammable mixtures.[150] Another effective solution can be the addition of gasoline or pentanes to methanol to enrich the vapor beyond the rich flammability limit. For example,

methanol with 15 percent gasoline would produce vapors beyond the rich flammability limit at temperatures above about 10°F.[148] Lower concentrations would be less helpful.[149] (See Chapter 7 for a discussion of methanol flammability and storage safety.)

A third safety concern relates to the toxicity of methanol. Methanol is colorless and nearly tasteless and odorless and therefore may not be recognizable to many people who are familiar with hydrocarbon fuels. This increases the potential for misuse of neat methanol. Adding hydrocarbons such as gasoline to methanol gives the fuel an unpalatable taste and odor and thus reduces the possibility of accidental poisoning.

FLEXIBLE-FUEL VEHICLES THAT CAN OPERATE ON ALCOHOL AND GASOLINE

Vehicles that can operate on either neat methanol or gasoline, or mixtures thereof, are currently being evaluated. The flexible-fuel concept has met with mixed enthusiasm from branches of the government and the automobile and oil industries. Proponents declare that mass production of flexible-fuel vehicles will promote consumer acceptance of methanol as a motor fuel and the development of a methanol distribution network. In turn the availability of neat methanol vehicles will be accelerated. Critics challenge the technical merits and question consumer acceptance of flexible-fuel vehicles. Those favoring neat methanol as a motor fuel argue that in order to achieve the perceived potential environmental and transportation fuel self-sufficiency benefits offered by methanol, engines and vehicle pollution controls should be optimized for neat methanol and not compromised to accommodate gasoline.

Several of the worldwide automobile manufacturers recognize the technical feasibility of the flexible-fuel car and have research and development programs in this area. The concepts of flexible-fuel cars are similar among manufacturers, but the nomenclature is not uniform. For example, manufacturers are using the following terminology: Ford, Flexible Fuel Vehicle (FFV); GM, Variable Fuel Vehicle (VFV); Chrysler, Gasoline Tolerant Methanol Vehicle (GTMV); and Volkswagen, Changeable Methanol Concept (CMC).[11, 136, 151, 152] All but Volkswagen specify M85 as the methanol fuel because of concerns about safety and cold starting; neat methanol is not acceptable.

Of these manufacturers Ford has the most field experience in the United States with methanol-powered cars and has published the most information on the flexible-fuel concept.[4, 5, 11, 153, 154] As of November 1987 six hundred sixty Ford-built methanol vehicles were on the road, thirty of which were FFV's.[155] An example of a Ford FFV is shown in Figure 33. The single fuel tank of the vehicle supplies the engine with an available fuel, from gasoline to M85, or mixtures of the two. A sensor in the fuel system detects the ratio of methanol to gasoline so that the fuel rate and ignition timing can be electronically adjusted for optimum performance, fuel economy, or emissions. The control system is very complex and relies upon newly developed technology. The onboard fuel sensor is based either on optical (refractive index) (Ford and Chrysler) or capacitive (GM) properties of the blend with final control via an oxygen sensor/feedback system.
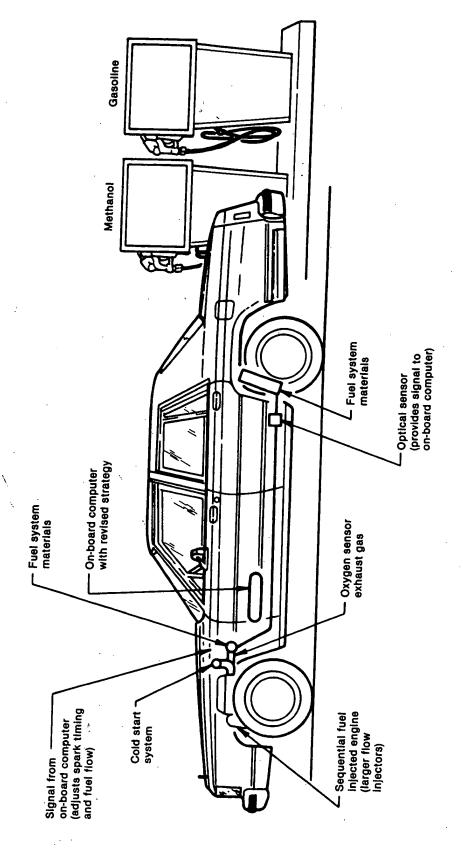
Engine efficiency that would be possible using methanol must be compromised to permit operation on gasoline in such vehicles. In development programs such as for the Ford FFV regular grade unleaded gasoline has been used to establish the basic engine compression ratio.[11] A design based on higher octane gasoline would allow an increase in compression ratio. At present premium grade represents the highest octane unleaded gasoline, and where available, generally has a minimum 91 $(R+M)/2$ octane rating. Premium unleaded would allow the compression ratio to be increased between one and two units above the ratio established for operation on regular grade unleaded, 87 $(R+M)/2$ octane rating.[129] However, this increase in compression ratio would provide only about 30 to 40 percent of the potential gain in energy fuel economy available if the compression ratio were increased to fully utilize the high octane of methanol.

The concept of the Volkswagen CMC vehicle differs from that of the FFV, VFV, or GTMV.[152] It incorporates a high compression ratio, 12.6:1, to take full advantage of the octane quality of neat methanol. Conversely, engine performance is degraded as necessary to allow emergency operation on gasoline. To accomplish this, the CMC vehicle has a complex dual fuel supply system; one for methanol and another with a smaller capacity for gasoline. With this system methanol produces maximum power with minimum energy consumption, but the emergency gasoline produces only 83 percent of the power and 73 percent of the efficiency obtained using methanol. The isolation of gasoline from methanol in the fuel system of the CMC eliminates the potential problems of excess vapor pressure caused by commingling fuels in a single fuel tank system.

GM is not optimistic about customer acceptance of vehicles compromised to run on both methanol and gasoline.[151] GM has stated that VFV's would present users with greater initial cost, increased complexity, shorter driving range, and poorer fuel economy than neat methanol vehicles. In its analysis GM views VFV's as hybrid vehicles for a transitional period. GM has stated that VFV's will likely not enjoy lasting acceptance in the marketplace and may face a fate similar to that of the diesel-powered passenger car in the United States.[151]

Major Unique Components

Gasoline

Methanol

Fuel system
materials

On-board computer
with revised strategy

Signal from
on-board computer
(adjusts spark timing
and fuel flow)

Cold start
system

Oxygen sensor
exhaust gas

Sequential fuel
injected engine
(larger flow
injectors)

Fuel system
materials

Optical sensor
(provides signal to
on-board computer)

Source: Reference 155.

Figure 33—Ford Flexible Fuel Vehicle

EVAPORATIVE AND EXHAUST EMISSIONS

Current knowledge concerning the characteristics of evaporative and exhaust emissions of alcohol-powered vehicles designed to meet U.S. emissions standards is based on data from a limited number of experimental and prototype vehicles. Brazil operates more than one million vehicles on neat ethanol but has no emissions standards. In the United States there is little interest in ethanol as a neat motor fuel due to the poor economics described in Chapter 3. Of all oxygenates, methanol has received most of the attention in the United States as a potential means to reduce regulated vehicle emissions for both spark-ignition and compression-ignition engines.

For spark-ignition engine applications of methanol practical considerations relating to cold engine starting and safety issues about flame luminosity and explosivity currently appear to support the use of near-neat methanol fuels such as M85. The State of California Energy Commission is currently seeking the participation of the automotive and oil industries in a 5-year demonstration program beginning in late 1988 that would include 5,000 light duty vehicles with the capability of operating on premium-grade unleaded gasoline, methanol-gasoline blend M85, and any combination thereof.[156] The vehicles would meet current California regulations for evaporative and exhaust emissions from gasoline vehicles plus an aldehyde limit. Much of the emissions control technology that has been developed for gasoline engines will be necessary for these vehicles. ARCO and Chevron have agreed to provide a total of up to 50 sites to dispense M85 blend. California also has neat-methanol demonstration projects for heavy-duty diesel vehicles, which will be mentioned later.

The potential for lower emissions from methanol-powered vehicles with spark-ignition engines is most attractive with respect to hydrocarbons. Neat methanol may offer advantages over gasoline for areas of the country that have severe urban air pollution problems because of its apparent lower activity in the photo-chemical reactions that result in "smog."[157-161] The EPA considers the reactivity of methanol to be 43 percent that of a (non-methane) hydrocarbon on a molecular comparison. It should be noted, however, that the data available for estimating the air quality impact of methanol vehicle emissions is very limited at this time. Durable in-use exhaust emission control has yet to be demonstrated for formaldehyde, which has very high photochemical reactivity. Also, multiday smog episodes may give adequate time for methanol to react to form ozone. The EPA and automakers have acknowledged

that the magnitude of the air quality benefits of methanol substitution are still somewhat uncertain and that estimates of the potential benefits would have to be updated as more data become available.[65, 162]

In addition to the potential for reducing smog methanol does not contribute to emissions of sulfur compounds which, although presently unregulated from mobile sources, are of concern environmentally. However, the exhaust emissions of CO and NO_x from optimized methanol vehicles have been found to be substantially the same as those from vehicles powered by gasoline.[4, 6]

Evaporative emissions of methanol appear to be controllable in a manner similar to the conventional charcoal canisters used for gasoline. However, the working capacity of a canister with methanol is less,[26] and there may be some questions about the long term effects of methanol on canister durability.[94, 95, 160] Emissions of evaporated methanol are toxic as discussed in Chapter 8 and their control must be considered for implications other than "smog" formation.

Neat methanol generally produces less evaporative losses from fuel-injected vehicles than gasoline.[4] However, when gasoline is blended with methanol, increases in vapor pressure occur as described in Chapter 2. Near-neat methanol blends, such as M90, M85, or other vehicle-tank blends that would be possible in fuel-flexible vehicles, can result in both evaporative and exhaust emissions of hydrocarbons from the gasoline fraction. The reactive evaporative emissions from vehicles fueled with methanol-hydrocarbon blends will consist mainly of the hydrocarbon component employed.

Ford conducted vehicle evaporative emissions tests that confirmed the effects of blends. The tests showed that mass missions with neat methanol were 40 to 65 percent o. .hose with gasoline.[4] Methanol with 15 percent Indolene produced mass evaporative emissions about the same as neat methanol in both 1985 FFV Escorts and a 1986 FFV Crown Victoria. However, a 50/50 methanol/gasoline blend in the Escorts increased emissions 140 percent over those with gasolines and 390 percent over neat methanol.[4]

Exhaust emissions control systems are needed to lower exhaust emissions from prototype vehicles designed to operate on either neat-methanol or near-neat methanol-gasoline blends. Theoretical benefits of reduced emissions of NO_x due to lower peak combustion temperatures when methanol is used instead of gasoline are not necessarily realized from optimized

methanol vehicle calibrations. Engine compression ratio increases, which are desirable to take advantage of the high octane of methanol and improve fuel economy, result in increased production of NO_x and unburned fuel emissions.[12] Most systems successfully employ three-way catalysts, closed loop control, and exhaust-gas recirculation as developed for gasoline engines.[8, 11, 136, 151, 152] Unburned methanol and CO appear to be lowered effectively by either oxidation-only catalysts or by three-way catalyst. However, due to lower exhaust-gas temperature with methanol, three-way catalytic converters do not operate as efficiently on methanol vehicle exhaust as on gasoline vehicle exhaust, particularly with respect to NO_x reduction.[163]

Although methanol vehicles may produce less reactive hydrocarbon emissions than gasoline vehicles, they can generate large amounts of reactive aldehydes and compounds such as formic acid. Aldehydes are also present in the combustion gases of gasoline engines, usually when mixture ratios are richer than stoichiometric such as during warm-up.[12] However, they are readily eliminated by exhaust catalysts. Aldehydes are difficult to measure in vehicle exhaust[101, 164] and are not currently regulated by the EPA, although they are under study. Tailpipe emissions from experimental vehicles operating on neat-methanol or near-neat methanol on the FTP driving cycle contain levels of aldehydes as much as ten times those observed in the exhaust from gasoline vehicles.[92, 135, 163, 164] As much as 95 to 98 percent of the aldehydes emitted is formaldehyde, a compound that has been identified as being highly active in the "smog" reactions, an eye irritant, and according to EPA, a probable human carcinogen. The EPA currently considers a molecule of formaldehyde to be 4.83 times as

reactive atmospherically as a molecule of (non-methane) hydrocarbon.[65]

Vehicle exhaust catalysts, either oxidation or three-way, can effectively control aldehyde and formaldehyde emissions from engines using either gasoline or methanol, especially at lean or stoichiometric air-fuel mixtures.[163, 165] Table 16 lists results from CRC programs that show that three-way exhaust catalyst systems lower aldehydes from neat methanol or an M90 blend by over 90 percent. However, the level of aldehyde after treatment was not as low as attainable with gasoline.[164] Much development work remains to optimize catalyst formulations for application to methanol vehicles. One automobile manufacturer has reported it was able to optimize a catalyst formulation and size, and lower aldehydes from M85 to the same levels obtained from gasoline with a three-way catalyst.[135] Another observed that certain base metal catalysts are as effective on methanol vehicles as noble metal catalysts used in three-way systems.[163] Formaldehyde emission control remains to be demonstrated for high mileage vehicles.

Exhaust catalyst requirements for controlling aldehyde emissions from methanol engines appear to be determined primarily by the lean-operating capability of the engine during warm-up.[135, 163] Mixture distribution, preparation, and vaporization have been identified as the factors that determine the ability to operate lean successfully.[8, 12, 140, 146] The Toyota lean-burn system incorporates a relatively sophisticated induction system that helps allow operation on M85 at mixtures 40 percent leaner than stoichiometric.[135] Through very lean operation the system minimizes the production of NO_x in the combustion process and can meet 1986 U.S. emission

Table 16—Formaldehyde Emissions

	Formaldehyde Emissions Average (grams/mile)[c]		
	Methanol-fueled:		Gasoline-fueled:
No catalyst	100% Methanol M90[b]	0.356 (2) 0.223 (1)	0.045 (5)
With oxidation-only catalyst	—	—	0.003–0.011 (unspecified number)
With 3-way catalyst	100% Methanol M90[b]	0.019 (2) 0.023 (1)	<0.002 (>4)

Notes:
[a] Source: Reference 164.
[b] M90 = 90% methanol + 10% Indolene HO-III gasoline.
[c] ( ) = number of vehicles tested.

standards for NO_x without exhaust-gas recirculation or a reduction catalyst. Although aldehyde emissions are higher in the lean-burn system, aldehyde levels have been lowered through oxidation catalyst modifications.

MATERIALS COMPATIBILITY

As discussed in Chapter 4, methanol is a highly polar material, and it chemically attacks elastomers and metals that perform satisfactorily with gasoline. Potential problems are corrosion of metals and the swelling or deterioration of plastics and elastomers. Both neat methanol and methanol-gasoline blends have been reported to attack the lead-tin coated steel (terne plate) that is used to fabricate domestic vehicle fuel tanks.[22] In one case involving a fuel-injected car, methanol effectively stripped the coating from the tank in two days. Severe corrosion developed on the exposed sheet steel, and the whitish, lead corrosion product partially plugged the fuel filter. A wide variety of corrosion inhibitors have been screened, including polyamide, polyamine, dithiocarbamate, thiophosphate ester, organic acid, sulfide, and selenide types, but as yet none have been found to be effective.[22, 111]

The inside of fuel tanks of cars destined to use gasoline-methanol blends are coated by some manufacturers with an aluminum-rich epoxy.[150] However, in service with neat methanol, this coating has blistered and flaked off after seven months. Type 304 stainless steel has been found to be compatible with methanol and is currently the preferred material for short production runs.[7, 166] Nickel-plated steel also has been found resistant to corrosion.[136] Blow-molded polyethylene would be a lower cost solution if the production volume were large enough to justify tooling costs.[150] The performance of high density polyethylene is excellent with neat or near-neat methanol but deteriorates and becomes permeable with gasoline-methanol blends.[150]

Anodic dissociation takes place where methanol is exposed to electrical potentials as in fuel level sensor units and in-tank electric fuel pumps. Because methanol is many times more electrically conductive than gasoline, a significant flow of current can take place, and metal is removed from the anode.[150] Coating the metals with polyolefin films appears to offer a solution to anodic dissociation.

Other investigators have found evidence of increased corrosion of copper, brass, bronze, magnesium, and die-cast zinc by methanol compared with gasoline.[18, 26, 111, 167] Metal corrosion is common in racing cars fueled with methanol, particularly if dissimilar metals are present and galvanic action is established.[121]

Carburetor and fuel gauge floats, both commonly made of plastics, have been noted to swell and gain weight in cars operated on methanol-gasoline blends.[150] This reduces their buoyancy and, for fuel gauge floats, causes falsely low fuel level readings. In one case a fuel pump failed after 4000 miles because the plastic pump head shrank and cracked.[168] Methanol may also attack methyl methacrylate parts, soften fiber gaskets, and dry and crack cork gaskets.[22] Racing cars use more expensive plastic parts to resist swelling or hardening of seals and diaphragms.[121]

Fluorocarbons, such as Vitons, are among the favored elastomers for conventional fuel system applications. They have good sealing characteristics over a wide temperature range and excellent resistance to hydrocarbons.[70] However, methanol attacks the Vitons and results in swelling and dimensional changes as high as 25 percent over a 24-week soaking period. There is not much change in hardness, however.[26] Increasing fluorine content has been found to improve the compatibility of fluoroelastomers with methanol.[155]

Methanol dilution of the engine lubricant was identified in one test program as the cause of valve stem O-ring embrittlement and valve stem seal softening,[150] which can result in increased oil consumption. In the same test program conventional cork gaskets used as seals for oil pans and rocker arm covers were found to crack and leak oil by capillary action.

ENGINE WEAR

Cylinder and piston ring wear are accelerated by the use of neat ethanol and methanol.[169] Methanol has been found to be particularly aggressive on cylinder wall wear at the upper end of the top piston ring travel, generating as much as seven times the wear rate as observed with unleaded gasoline.[170] Startup wear is caused by metal to metal contact resulting from the washing away of the normal oil film by liquid alcohol during starting. Startup wear occurs when very long cranking times are required to start the engine.

The wear associated with the use of methanol during warmed-up engine operation has been identified as a type of corrosive wear.[171] The increased wear has been theorized to be a result of formic or performic acid formation during combustion and the direct attack of the acid on the iron.[171-173] New formulations of lubricating oil additives are being sought to control corrosive wear of the upper cylinder. Service station engine oils that meet the requirements for conventional gasoline engines have been found inadequate for methanol engines, and special formulations are specified for field tests.[7, 166]

Even with special lubricants, however, most methanol vehicle manufacturers recommend more frequent oil changes than for gasoline vehicles.[173,174]

Fuel contaminants, such as chlorine or peroxides, have been found to significantly increase corrosion and wear in a methanol engine.[172, 175] No widely accepted specifications exist for fuel-grade methanol. The level of contaminants ultimately defined as acceptable will have a significant impact on the design of fuel systems for methanol vehicles.

Modifications to methanol engine components, such as the use of chrome-plated piston rings, have been found to reduce wear in methanol engines.[173, 175, 176] Chrome-plated rings have been used in production vehicles to improve durability.[177]

Alcohol Fuels for Compression-Ignition Engines

Although alcohols are not ideal as compression-ignition engine fuels from either the physical or thermodynamic standpoint, they do offer certain advantages in diesel applications. Exhaust emissions of particulates, sulfur compounds, and NO_x are major concerns to diesel engine manufacturers. These can be reduced or mitigated by the use of alcohol. For some time alcohol has been recognized as a means to reduce diesel smoke.

Alcohols cannot be used in conventional diesel-powered vehicles without modifications to the fuel system and engine. Simple blends of diesel fuel with over 30 percent ethanol are impractical because water tolerance and phase separation problems are more likely with diesel fuel than with gasoline (see Chapter 2).[178, 179] Methanol cannot be considered for simple blends with hydrocarbon diesel fuel because it is insoluble and must be handled separately with a dedicated fuel system. The low viscosity and lubricity of alcohols present special wear problems in conventional diesel fuel injection systems where the fuel is relied upon to provide lubrication of the high pressure pumps and injectors. About 15 percent ethanol decreases the viscosity of a typical ASTM 2-D fuel from 2.4 centistokes to below the viscosity limit for ASTM 2-D, and about 62 percent ethanol in a typical fuel results in a blend with viscosity below the limit for ASTM 1-D fuel.[180]

The cetane numbers of methanol and ethanol are extremely low, ranging from 0 to 8, compared with generally acceptable values for diesel fuels in the range of 40 to 50 cetane.[181-183] Cetane improvement for methanol and other alcohols has been demonstrated through the addition of nitrated compounds.[184] For ex-

ample, about 15 to 16 percent by volume cyclohexyl-nitrate can increase the cetane of methanol and ethanol to a level of 40 cetane, and it has been demonstrated that the mixture produced slightly better specific fuel consumption than diesel fuel at full and part load without any measurable exhaust smoke.[14]

The heating value differences between alcohols and diesel fuel must be considered when examining the cost effectiveness of additives for cetane improvement. On a volumetric basis 2.28 times as much methanol is needed for the same heating value as diesel fuel. Ethanol requires 1.69 times as much volume. Compared on a basis of equal heating value or power output, the true additive requirement to treat methanol would be about 36 percent by volume of diesel fuel required. There have also been reports of mechanical problems with the use of ignition-improved methanol in heavy-duty diesel engines.[185] This methodology has little commercial attractiveness, and the direct approaches using neat alcohol have less economic disincentives.

Fumigation of alcohol into the intake air of diesel engines was found to be one way to increase engine power without exceeding the exhaust smoke limit.[186-190] Various means that have been used to introduce alcohol into the airstream include heated vaporizers, carburetors, manifold injectors, and mist generators. The basic objective is to augment diesel fuel energy release with as rich an alcohol-air mixture as the combustion process will tolerate without quenching or misfire. With fumigated methanol engine combustion is usually satisfactory with up to about 60 percent by volume methanol or about 26 percent of the total heat input.

Other experimental dual fuel schemes employ a separate injection system for alcohol in both pre-chamber and open chamber engines.[179, 191-193] The benefits of dual injection are increased thermal efficiency and reduced exhaust emissions of NO_x and particulates.[14, 191, 194] Increased aldehyde emissions have not been found for this type of engine compared with unmodified diesel engines.[191] However, the complexity of dual fuel injection control systems has led to development of engines that can utilize neat alcohol as the sole fuel.

The State of California Energy Commission has concluded that neat methanol can be as cost effective an emissions control element for diesels as any vehicle hardware. It is sponsoring demonstration projects in several medium- and heavy-duty applications of both two- and four-stroke cycle diesel engines in truck, bus, and farm tractor service.[195]

Komatsu in Japan, DDC in the United States, and M.A.N. in West Germany have developed versions of diesel engines that operate on neat methanol. The Komatsu derivation is based on a prechamber design that has been field tested in tractors.[196] Both the DDC and the M.A.N. engines are being tested in transit bus service using neat methanol.[6] The DDC engine is a two-stroke cycle engine that incorporates glow plugs to assist ignition at light loads and an electronically regulated hot intake air system for high output operating conditions.[197, 198] Initial difficulties with the DDC approach included poor driveability and fuel injector failures.[6]

The M.A.N. methanol engine features a sparkplug ignition system to assist combustion and has been developed over a period of 16 years.[199, 200] It is based on a conventional open combustion chamber, four-stroke-cycle engine. M.A.N. has observed improved thermal fuel economy for the methanol-powered engine in laboratory tests and confirmed the finding in bus field tests where up to 5 percent improvement in thermal fuel economy has been shown.[6, 200] Also, a marked reduction in NO_x emission of up to 50 percent and the elimination of exhaust particulates and smoke have been reported. Combustion of methanol in a spark-assisted diesel engine has been found to be mainly flame propagated, similar to that in a gasoline engine.[201] Accordingly,

diesel engines must be redesigned to optimize basic elements, such as compression ratio and fuel injection and ignition systems, in order to utilize methanol as efficiently as diesel fuel.

Table 17 lists the results of exhaust emissions tests of buses powered by the DDC and M.A.N. methanol diesels.[198] Compared with typical diesel bus emissions of particulates, both buses were at least 44 percent lower. In addition to the virtual elimination of particulates through the use of methanol, the exhaust catalyst system used on the M.A.N. bus lowered carbon monoxide emission and emissions of methanol and aldehydes. The durability of exhaust catalysts as well as the reliability of both the DDC and the M.A.N. methanol engines in transit bus service remain to be determined.

While the substitution of methanol for diesel fuel appears attractive to reduce exhaust particulate and NO_x emissions, it remains to be seen what combination of fuel and emissions control technology is the most cost-effective to meet heavy-duty engine emission limits. It is possible that modifications to diesel fuel composition, such as sulfur reduction, along with particulate traps and other control hardware may in the long-term be less costly to the consumer than methanol substitution and exhaust catalysts.[202]

Table 17—Comparison of Emissions From Methanol–Diesels to Emissions From Diesels (Chassis Dynamometer Tests on CBD[b] Cycle)

	MAN	DDC	Typical Diesel
HC,[c] g/km	0.53	75.0	1.7–2.5
CO, g/km	0.48	55.0	10–18
NO_x, g/km	8.80	4.9	14–19
Particulate, g/km	0.06	0.96	1.7–3.9
Aldehyde, g/km	0.10	1.20	Not detected
Methanol, g/km	0.35	62.0	Not detected
Diesel fuel equivalent economy, km/kg	2.2	1.5	1.8–1.9

Notes:
[a]Source: Reference 198.
[b]CBD — Central Business District.
[c]Corrected for FID response factor of 0.8.

CHAPTER 6—ALCOHOLS AND ETHERS IN NONAUTOMOTIVE FUEL USES

Marine Applications

Alcohol blends are generally not recommended for use with either outboard or inboard marine engines. If alcohol blends must be used, they should be used with extreme caution.[203-205] The use of methanol or methanol

blends is generally prohibited by marine engine manufacturers. However, the use of ethanol in concentrations up to 10 percent is permitted by most manufacturers with the strong caution that fuel systems must frequently be inspected for leaks and other problems such as metal corrosion and deterioration of elastomers. Several

reasons for these positions are described in the paragraphs that follow.

PHASE SEPARATION

Some manufacturers are concerned about phase separation above all other problems because of the presence of moisture in the boating environment. These manufacturers are cautious regarding ethanol blends and are absolutely against using methanol blends because of their increased tendency to phase separate when exposed to water.

In a marine environment contact with water is difficult to prevent, and some boats are left for long periods without use. Because blends are hygroscopic, even contact with humid air can cause phase separation.

CORROSION/ELASTOMERS DETERIORATION

The materials that are currently used in most fuel systems were not designed for exposure to alcohols or alcohol blends. Therefore, fuel leakage or vapor loss can occur as a result of metal corrosion and effects on elastomers with a consequent fire hazard.[204] If future fuel systems for alcohol fuels or blends are required, they can be designed to eliminate these problems.

Some engine manufacturers comment that total fuel system design is not under their control because of the boat builder's design. However, if a fuel problem develops, the engine manufacturer is sometimes questioned. For this reason some manufacturers take a cautious position.

FUEL VOLATILITY

Some alcohol blends, for example, gasohol, are made by adding alcohol to gasoline that has generally been manufactured according to ASTM D 439 specifications. The final blend has higher vapor pressure because of blending properties of the alcohols that were discussed in Chapter 2. Higher volatility may cause fuel pump vapor lock under certain conditions, which could cause hard starting or engine stalling.

OCTANE QUALITY

As previously discussed in Chapter 4, in some high-speed, high-power applications the apparent antiknock quality of alcohol blends, as indicated by Research and Motor method octane ratings, is not realized. Knock, piston seizure, and piston-ring sticking have occurred in some of these engines.

Fuels that contain MTBE or TBA, as permitted by the EPA, are not considered subject to the problems listed

above. Gasoline-MTBE or gasoline-TBA blends have not been addressed by marine engine manufacturers. At this time no firm written position has been taken to allow or disallow these blends for marine use. The blends simply are not referred to in the owner's manuals. It is unlikely that a recommendation will be made against their use, since their properties are similar to gasoline.

Piston Engine Aircraft

Gasohol and other alcohol blends are not recommended by the engine or airframe manufacturers for use as fuels for piston engine aircraft. After sufficient testing certain automotive gasolines have been approved by the Federal Aviation Administration (FAA) for specific engine models.[206] In such cases the minimum antiknock index level is specified by the FAA per ASTM D 439, and the approval applies only to the engines tested. Gasohol, regardless of whether it meets ASTM D 439, is not considered automotive gasoline for purposes of FAA approval.[207]

Manufacturers of aircraft and aircraft engines specify that the fuel used meet the ASTM Aviation Gasoline Specification D 910. Certain engines may operate satisfactorily on properly blended automotive fuels that contain alcohol or other oxygenates if the finished fuels meet ASTM D 439 specifications and have adequate octane quality and cleanliness. Most gasoline-ethanol blends are splash blended and do not normally meet ASTM D 439 specifications.

Alcohol blends can cause problems with elastomers and aluminum fuel tanks because the fuel systems were not designed to operate with alcohol fuels. Phase separation is also a possible hazard with alcohol blends.

Some experimental work has been done with 50/50 percent by volume methanol-ethanol blends as a substitute fuel for aircraft designed to run on aviation gasoline. A major disadvantage is the reduction in range.[208]

Motorcycles

Some motorcycle manufacturers do not address the use of alcohol or other oxygenate blends in their owner's manuals. One motorcycle manufacturer specifically recommends against the use of alcohol blends in its owner's manual.[209] If ethanol or methanol blends must be used, the manual recommends no more than 10 percent ethanol or no more than 5 percent methanol, provided a cosolvent and corrosion inhibitor are also used.

Snowmobiles

Snowmobile manufacturers generally permit the use of up to 10 percent ethanol in a gasoline blend but recommend against the use of methanol or methanol blends.[210] However, small amounts of methanol for anti-icing are not necessarily prohibited. The principal concern with using methanol blends is phase separation and air-fuel mixture enleanment.[210] Snowmobile manufacturers currently do not address the use of other oxygenated fuel components such as MTBE.

Lawn Mowers and Small Tractors

Some manufacturers of lawn mowers and small tractors take no position on oxygenated fuels in their owner's manuals.[211] Others recommend against the use of gasoline-alcohol blends such as gasohol. In such cases, if alcohol blends must be used, they must not contain more than 10 percent ethanol, and blends containing methanol must never be used.[212]

Other manufacturers permit the use of ethanol or methanol blends but caution about fuel leakage and deterioration of certain materials.[213] At least one manufacturer recommends against the use of any gasoline substitutes.[214]

In addition to the usual alcohol problems of phase separation one major manufacturer reports corrosion of aluminum parts, including cylinder bores, when using ethanol blends.[215] The same manufacturer reports no problems with oxygenated materials such as MTBE as long as they are present within EPA limits.

Chain Saws

The manufacturers of chain saws generally recommend against the use of any kind of alcohol or alcohol blend with gasoline.[216] Some manufacturers are concerned about phase separation because the separated phase of water and alcohol will not lubricate their two-stroke cycle engines, and piston sticking will occur. In addition chain saws frequently have aluminum or magnesium fuel tanks that can be corroded by the water-alcohol mixture after phase separation has occurred.

Snow Blowers

At least one major manufacturer of snow blowers takes a very strong position against methanol or methanol blends and states that they should never be used in any form.[217] However, the same manufacturer permits ethanol blends in concentrations up to 10 percent.

Stationary Power Sources

Neat or near-neat alcohol fuels can be used advantageously in turbines and boilers because of their lower flame luminosity and combustion temperatures. The principal requirements in using alcohols are increased fuel storage and pump capacity and a modified nozzle size/spray pattern that compensates for the reduced energy content and lower viscosity of the fuel.

Methanol is an extremely clean burning fuel when compared with conventional industrial fuels other than natural gas. The combustion of neat methanol generally will result in the lowest NO_x emissions and virtually no sulfur or particulate emissions. Sulfur emissions are non-existent since, unlike liquid petroleum-based fuels, methanol contains no sulfur. Particulate emissions are also low with methanol and are comparable to those with natural gas.[218]

In tests carried out in turbines and boilers without emissions controls, neat methanol fuel reduced NO_x emissions to levels significantly below those with middle distillate fuel or natural gas. They were also lower than the emissions in tests where water injection was used with middle distillate fuel or natural gas. NO_x emissions with methanol were lower because of cooler flame temperature.[219] In addition gas turbine testing with methanol fuel indicated a slight gain in power output over that obtained with middle distillate fuel.[220] Testing also indicated that a methanol fuel turbine would be internally cleaner than a turbine operated on middle distillate fuel for a similar period of time.

Although not serious obstacles, methanol has a low heating value and low lubricity compared with distillate fuel. Fuel systems would need to be designed to accommodate methanol's low flash point and wide flammability range. Extreme care would be required in the shipping and storage of methanol to prevent salt water (sodium) contamination. Sodium will cause corrosion of turbine nozzles and blades.

In 1987 experimental data was reported on the first use of methanol with oil or natural gas in the dual fuel combustion process.[221] Dual fuel combustion is a technique discovered by Jones and Mansour[222, 223] to reduce the amount of NO_x emitted from power boiler burner combustion. The technique involves burning a fuel containing less nitrogen in the top row of burners over a fuel containing more nitrogen in the bottom row of burners. The technique works particularly well with methanol because a) methanol contains no fuel-bound nitrogen, b) methanol's theoretical flame temperature is lower than fuel oil or natural gas, and c) methanol

allows fuel-lean combustion in the upper burner region, permitting fuel-rich (less NO_x) combustion in the lower burner region. The NO_x emission reductions reported using this technique in a utility boiler at a level of 35 megawatts are summarized in Figure 34. Preliminary data on this type of equipment indicates that for good flame stability, 30 percent methanol should be the minimum concentration of methanol used. Experiments in which one of the six methanol burners was shut down (a procedure known as "staging") showed the potential for even further NO_x reductions.

Power plants are under development in which methanol and electric power are coproduced using an integrated coal gasification combined-cycle plant. Synthesis gas from the coal gasification process is used to produce methanol in a "once through" process without recycle. The unconverted synthesis gas is utilized in combined-cycle equipment to produce electricity. The methanol, which is easily stored, is used to fuel gas turbines to provide additional power during peak demand periods.[219]

Notes:
1. Asterisk indicates dual-mode combustion.
2. Source: Reference 221.
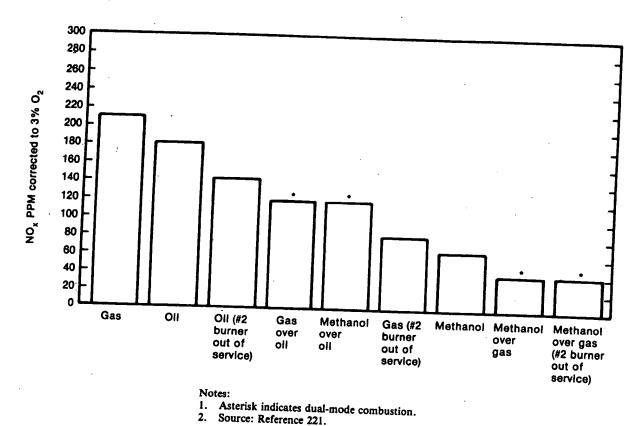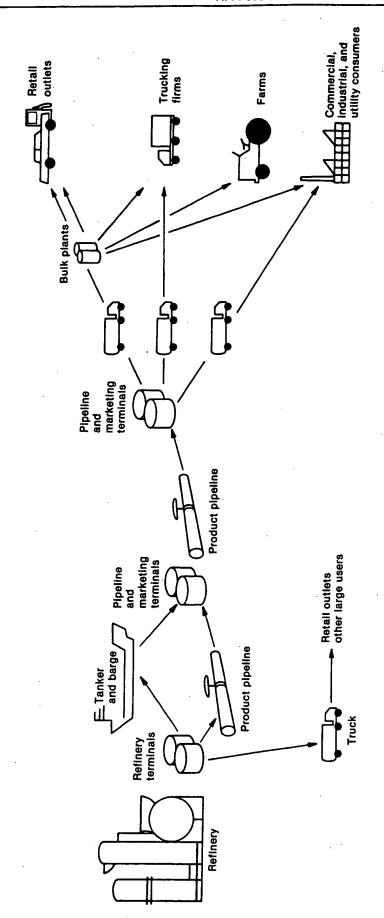
Figure 34—Comparison of Stationary Combustion NO_x Emissions

CHAPTER 7—DISTRIBUTION AND STORAGE OF ALCOHOLS, GASOLINE-ALCOHOL BLENDS, AND GASOLINE-ETHER BLENDS—TRANSPORTATION, MARKETING, SAFETY AND FIRE PROTECTION, AND MEASUREMENT

Current Gasoline Distribution System

The current gasoline storage and distribution system is illustrated in Figure 35 and consists of a) refineries, b) refinery terminals, c) products pipelines, d) product tankers and barges, e) rail, f) pipeline and marketing

terminals, g) bulk plants, h) tank trucks, and i) service stations or retail outlets.[224] The majority of gasoline today (55 to 60 percent) is shipped from refineries by pipeline to pipeline and marketing terminals. About 35 percent of gasoline is shipped from refineries by barge and tanker, and the remaining 5 to 10 percent is shipped

Source: Reference 224.

Figure 35—Typical Gasoline Distribution System

by truck.[225-228] Gasoline is currently not shipped by rail in any significant amount. However, rail is often the major mode of transporting oxygenates to blending locations. From pipeline and marketing terminals almost all gasoline is moved by truck to bulk plants, service stations, and major users such as farms and large commercial customers.

The affinity of gasoline-alcohol blends for water generally makes alcohol addition at any point other than truck loading at terminals more difficult (see Figure 35). Other points further upstream in the distribution system can be exposed to water, and therefore phase separation could occur if gasoline-alcohol blends were introduced at any other point in the system. However, gasoline-alcohol blends have been successfully shipped by pipeline as part of commercial marketing of finished gasoline.[38, 229-232] This was done, however, with extraordinary concern for quality control and dryness of the system and involved capital investments. Water contamination of gasoline-alcohol blends presents a major and costly potential problem in the distribution of these fuels.

There are many complexities that tend to make pipeline shipment of gasoline-alcohol blends more difficult. For example, refineries may blend gasolines from components continuously and deliver directly to a pipeline, or they may batch-blend the gasoline into shipping tanks. Long pipelines may have intermediate "breakout" tanks that are necessary for efficient operation of the pipeline. Most have multiple terminals or delivery points along the line.[38] Refinery shipping tanks, pipeline breakout tanks, terminal, and bulk plant tanks are wet; that is, water is always present. For example, many gasoline tanks are equipped with uncovered floating roofs that limit evaporation but do not completely exclude water. In addition products are saturated with water when they leave the refinery. This is no problem with gasoline because any water from rainfall or snowfall leaking into the tank or condensing out of the product separates readily from the gasoline. The "water bottoms" that collect are drained from the tank as part of the routine maintenance activities of the pipeline or marketing terminal. However, water that enters a tank holding gasoline-alcohol blends could exceed the capacity of the blend to dissolve water. If this occurred, the water could extract the alcohol from the gasoline-alcohol blend, and phase separation would result. The resulting alcohol-water mixture would require more extensive waste treatment than for water alone. Chapter 2 provides information on the water tolerance and sensitivity of various gasoline-alcohol blends.

Because gasoline-MTBE blends are compatible with the current storage and distribution system and have a low affinity for water, MTBE is usually added at the refinery, and the blend is shipped by pipeline or any of the other modes of transportation as shown in Figure 35. MTBE can also be added at the marketing terminals. Although gasoline-MTBE blends are compatible with most elastomers found in automotive fuel systems and gasoline storage and distribution systems, it should be noted that fluorocarbon elastomers such as Viton A should not be used in contact with neat MTBE, as 100 percent MTBE has been found to degrade these materials.[118, 233]

Distribution and Storage of Gasoline-Alcohol Blends—Refinery, Pipelines, Terminals and Service Stations

TRANSPORTATION SYSTEMS

If gasoline-alcohol blends currently approved under EPA rules and regulations were to be distributed starting at the refinery, which would be the case if the volume to be supplied required pipeline shipment, important changes or additions would have to be made to each mode of transportation—pipeline, tanker, barge, rail, and truck. Because there are differences between requirements for storing gasoline and requirements for storing gasoline-alcohol blends, changes to pipeline storage terminals would also be necessary.[234, 235] More widespread use of gasoline-alcohol blends, moreover, could also require additional pipeline storage capacity.

Because of the affinity of alcohol for water, the largest change required for pipeline transportation of gasoline-alcohol blends could be installation of dehydrating equipment.[236] Complete pipeline dehydration would be required for large multiple shipper–multiple product systems because conventional hydrocarbon products and alcohol blends would be handled by the same pipeline. In such cases all petroleum products that are shipped by the pipeline would have to be dehydrated, and the pipelines might have to be cleaned much more frequently. Gasoline-alcohol blends can also interfere with the protection offered by commonly used corrosion inhibitors in pipeline systems. Moreover, pipelines may have to install additional tankage, install dome roofs on floating roof tanks, and install additional product testing instrumentation. Another concern is contamination of other products, especially aviation turbine fuel, with alcohol. Aviation turbine fuel contaminated with alcohol, besides being an illegal fuel, would carry increased amounts of dissolved water through the filter/coalescer units into the fuel tanks of

aircraft. When the fuel cools down at high altitude, the water/alcohol will separate from the fuel and can cause stress to the fuel system components (corrosion of metals, leakage of sealants, and incompatibility with internal fuel bladders).

Shipping gasoline-alcohol blends by barge or ship would require replacement of tank coatings in some vessels, replacement of valve and pump seals with materials compatible with gasoline-alcohol blends, and other maintenance and product quality assurance operations. Replacing single-skin barges with double-bottom barges may also be required. These same concerns must be addressed with large shipments of neat alcohols and ethers.

Blending gasoline and alcohol at the refinery terminal or at pipeline terminals requires shipping the alcohol from the production site by rail, truck, or barge to the facilities. Additional tankage may also be needed for storing the alcohol for blending. Each refinery may need rail off-loading facilities, including tankage. Computerized in-line blending facilities are likely to be added to terminals where blending of gasoline and alcohol occurs.[237]

MARKETING TERMINALS AND BULK PLANTS

Gasoline-alcohol blends currently approved under EPA rules and regulations can generally be stored at existing marketing terminals and bulk plants after some equipment modifications.[234, 235] If the volume supplied necessitates, additional tankage would have to be installed.

Gasoline-alcohol blends should be stored in a tank with a fixed roof and an internal floating cover.[234, 235] Facilities not so equipped should be modified. Extreme care must be taken to ensure that any tank lining is compatible with the gasoline-alcohol blend. If blending occurs at the terminal, additional tankage may also be needed for storing the alcohol for blending. For terminal blending of gasoline and alcohol in-line blending is recommended.

The following list summarizes some of the factors that must be considered in order to convert an existing marketing terminal to handle gasoline-alcohol blends currently approved by EPA rules and regulations:[236]

a. Receiving facilities (valves/pump seals).
b. Storage tanks.
   1. Replace floating roof when required (that is, from aluminum to steel).
   2. Cover floating roof.
   3. Evacuate, clean, and inspect.

c. Loading facilities — pumps, valves.
d. Vapor recovery increased capacity.
e. Inline blending facilities.
f. Additional fire and safety facilities/alcohol-water bottoms drawoff.
g. Oily water/waste disposal (some form of environmentally acceptable waste water treatment).

RETAIL FACILITIES — SERVICE STATIONS

Gasoline-alcohol blends currently approved under EPA rules and regulations can generally be handled at existing service station facilities after some maintenance and equipment modifications.[234, 235, 237] Service station tanks must be cleaned and dried before being used for gasoline-alcohol blends, and extra precautions must be taken to keep water from entering the tank after use begins. Water from rainfall or snowfall leaks can enter service station storage tanks through filler ports. Water can also enter as humid air is drawn into tanks during diurnal breathing cycles and when fuel is withdrawn from the tanks. This has not been a problem in the use of gasoline-alcohol blends because of their capacity to dissolve some water. Once dry, gasoline-alcohol systems have the potential to keep themselves dry with continuous use of the gasoline-alcohol blends. Care must be taken to ensure that any storage tank lining is compatible with gasoline-alcohol blends and alcohol/water tank bottoms. Filters must be installed in the final dispensing system to ensure the delivery of clean product, since gasoline-alcohol blends will loosen rust and dirt deposits throughout the system. Depending on the age and materials in the service station dispensing pump, the meters will require either replacement or recalibration when gasoline-alcohol blends are first introduced.

The following list summarizes some of the factors that must be considered in order to convert a retail service station to handle gasoline-alcohol blends currently approved by EPA rules and regulations:[236]

a. Storage tank compatibility.
b. Overfill protection.
c. Pumps and line leak detectors.
d. Pump meter replacement or recalibration.
e. Dispensers and filters.
f. Alcohol-resistant materials — hoses, seals, nozzles.
g. Storage tank cleaning and drying.
h. Protection from water contamination — dryers on vent lines and pressure vacuum vents, fill cap O-rings.
i. Application of special signs and decals.

SAFETY AND FIRE PROTECTION

The safety and fire protection precautions for storing and handling EPA approved gasoline-alcohol blends are similar to those for gasoline. All applicable government and industry standards should be followed. Although there are similarities in extinguishing fires involving gasoline-alcohol blends, some important differences exist. API Recommended Practices 1626 and 1627 provide technical guidance on safety and fire protection procedures for gasoline-alcohol blends at service stations and distribution facilities.[234, 235] API Publication 2300 treats differences in the selection and use of firefighting foams.[238]

In addition to safety and fire considerations for the gasoline-alcohol blends precautions and safety procedures for handling the alcohol at the point of blending must be followed, regardless of whether blending occurs at the refinery terminal, pipeline terminal, or marketing terminal. At those facilities handling alcohol for blending with gasoline, it is recommended that a polar-solvent (alcohol-resistant) foam be provided.[236] In case of a fire local authorities may not be certain what fuel is involved. The polar-solvent (alcohol-resistant) foam is suitable for all the situations that will likely be encountered and can eliminate uncertainty as to selection of the agent. This provides maximum protection. The water/alcohol bottoms drained from storage tanks may be flammable. Appropriate precautions should be taken during handling and disposal.

MEASUREMENT/INVENTORY ACCOUNTING SYSTEM

Inventory accounting systems may be compromised, in some instances, by the presence of gasoline-alcohol blends in the distribution and storage system.

Product must be inventoried through a series of measurements during product distribution to ensure accurate custody transfer and compliance with loss prevention systems. The presence of alcohols in fuels compromises the accurate determination of volume adjusted for temperature because alcohols do not have the same density and coefficient of expansion relationship as hydrocarbons. A further compromise exists because of the volume growth that occurs when alcohol is added to gasoline (see Chapter 2). These measurement problems would be most important for bulk transfers involving pipeline measurements and associated storage. There is less concern for small transfers such as at truck transfers, small tanks, or bulk plants.

Currently, no generalized volume correction factors for gasoline-alcohol blends exist. Although no extensive assessment has been made to determine the loss of accuracy that occurs when using the gasoline volume correction factors for gasoline-alcohol blends, one study of a gasoline-ethanol blend did show that the increased error for correcting volume of that blend to 60°F was about 0.03 percentage points.[239]

Evaporation losses can be calculated for gasoline-alcohol blends stored in internal floating roof tanks using API Publication 2519[240] and prediction models.

Distribution and Storage of Neat or Near-Neat Alcohols—Refinery, Pipelines, Terminals, and Service Stations

TRANSPORTATION SYSTEMS

Transportation and storage capacity are primary considerations in the application of neat or near-neat alcohols as fuels. Methanol has about half the energy content of gasoline, and ethanol has about two-thirds the energy content of gasoline. As discussed in Chapters 2 and 5, it will most likely require about 1.8 gallons of neat methanol fuel to provide the same driving range as 1 gallon of gasoline. The greater quantities of alcohol needed to provide the same vehicle driving range could not be distributed and stored without the addition of facilities for each mode of transportation (pipeline, marine, truck, and rail) within the current distribution system.

In addition to substantially increased distribution and storage capacity replacing gasoline with neat or near-neat alcohols requires the same changes to the transportation system as those discussed in the previous section for gasoline-alcohol blends. The following list summarizes some of the factors that must be considered in order to transport neat or near-neat alcohol fuels:[236]

a. Pipelines.
   1. Capacity and throughput.
   2. Dehydration equipment.
   3. Materials compatibility.
   4. Terminal tankage, tank roofs, product testing, inline blending, and truck loading facilities.
   5. Maintenance.
   6. Contamination of other petroleum products by alcohols.

b. Trucks.
   1. Truck capacity for transport from refinery and terminal.

2. Capacity loss due to heavier payload.

c. Rail: capacity for transport to refinery or terminal.
d. Marine (ship transportation).
   1. Capacity.
   2. Materials compatibility (seals/valve packing, maintenance).
   3. Product quality (coatings, new or renew).
   4. Segregated ballast retrofit (hazardous substance).

e. Marine (barge transportation).
   1. Material compatibility.
   2. Double bottoms.

MARKETING TERMINALS

As previously noted, the distribution and storage of neat or near-neat alcohols from marketing terminals would require substantial increases in storage capacity to supply the equivalent vehicle driving range requirements of gasoline. Storage facilities for neat or near-neat alcohols, like those for blends, must be equipped to prevent water from entering. This requires fixed roofs with internal floating covers.[234]

For the supply of near-neat alcohol the alcohol can be transported to the terminal and then blended, or the near-neat alcohol can be shipped to the terminal by pipeline from the refinery already blended. Either case requires additional storage tankage. The capacity of vapor recovery systems would need to be increased. Truck loading rack facilities would also be required. In-line blending facilities would be required for terminal blending of near-neat alcohols.

Care must be taken that all storage facility materials are alcohol compatible. Environmentally acceptable treatment systems for waste waters are also a concern. Water-contaminated alcohol fuels present a major and potentially costly problem in the distribution of these fuels. Such off-specification material is unmarketable and must be either disposed of or reprocessed in some way to remove the water.

The following list summarizes some of the factors that must be considered to convert an existing marketing terminal to handle neat or near-neat alcohol fuels:[42, 234, 236]

a. Receiving facilities (valves/pump seals).
b. Storage tanks.
   1. Replacement of floating roof when required (that is, from aluminum to steel).
   2. Evacuation, cleaning, inspecting, and refilling.
   3. Valve seals.
   4. Floating roof seals.

   5. Floating roof cover.
c. Loading facilities — pumps, valves.
d. Vapor recovery capacity and material compatibility.
e. Inline blending facilities.
f. Additional fire and safety facilities.
g. Oily water/waste disposal — some form of environmentally acceptable waste water treatment.

RETAIL FACILITIES — SERVICE STATIONS

At retail facilities neat or near-neat alcohol fuels would most likely be handled through the addition of a separate storage, pumping, and dispensing system. In addition to all the earlier described considerations for storing neat or near-neat alcohols the service station underground storage tank and lines would require some form of secondary containment under the proposed EPA underground storage tank regulations.

The following list summarizes some of the factors that must be considered when installing a new facility for neat or near-neat alcohols or for retrofitting or converting an existing system to be alcohol compatible:[42, 236]

a. Storage tanks and underground lines with secondary containment system.
b. Piping (vents, fills, product lines).
c. Overfill protection.
d. Fillpipe spill containment.
e. Stage I vapor recovery.
f. Pumps and line leak detectors.
g. Dispensers.
h. Alcohol resistant materials — tank hoses, seals, nozzles.
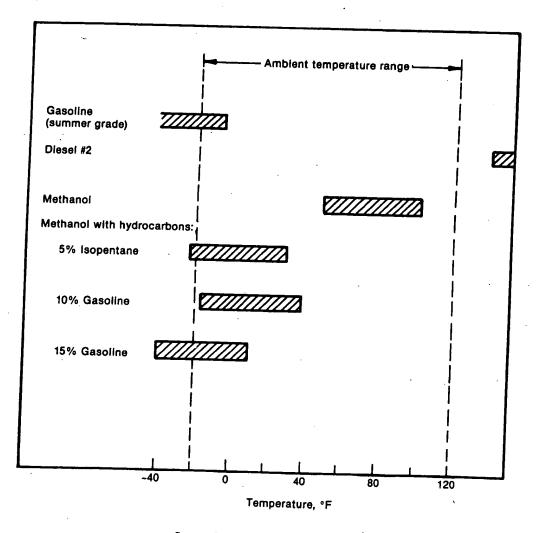
SAFETY AND FIRE PROTECTION

Fires involving neat or near-neat alcohol fuels present special fire fighting problems.[236] These fires require the use of alcohol-resistant foam concentrates or dry chemicals. Trends in local codes suggest that service stations dispensing neat or near-neat alcohol fuels may require maximum protection. References 234 and 238 provide technical guidance on the safety and fire protection considerations for alcohol fuels. Alcohols are generally stored in tanks with internal floating covers. However, the flammable and combustible liquids code, NFPA-30,[241] does not prohibit the use of cone roof tanks for this application.

The relative fire hazards associated with alcohols and gasoline can be compared by means of the properties listed in Table 18.[2] Figure 36 compares the vapor space flammability limits for methanol and methanol blended with various liquid fuels.[149] The vapor space over

Table 18—Comparison of Properties Relating to Fire Hazards for Alcohols and Gasoline

Property	Methanol	Ethanol	Gasoline
Flash point, °F	52	55	-45
Autoignition temperature, °F	867	793	495
Flammability limits, volume percent	7.3–36	4.3–19	1.4–7.6
Vapor pressure at 70°F, psi	1.9	0.8	4.8
Vapor pressure at 100°F, psi	4.6	2.3	8–15
Concentration in saturated air at 68°F, volume %	13	5.4	25–50

Source: References 148 and 149.

Figure 36—Vapor Space Flammability Limits Over Liquid Fuels

methanol will normally be in the flammable range at bulk liquid temperatures between about 45°F to 110°F. When blended with hydrocarbon fuels, the vapor space flammability limits of methanol approach those of gasoline. As discussed in Chapter 5, methanol presents a special safety hazard because it burns without much visibility. Hydrocarbons blended with methanol have been found to effectively increase flame luminosity.[26]

Ethanol and methanol tanks should be located within separate dikes, or if located within a common dike, intermediate dikes or proper drainage should be provided.

Special foam chambers and modified foam application techniques are required for protecting neat or near-neat alcohol tanks. Higher foam application rates may be required for extinguishing tank and dike fires. Subsurface foam injection is not effective in most polar fuels and is not recommended for extinguishing either ethanol or methanol storage tank fires.

CHAPTER 8—GROUNDWATER AND TOXICITY EFFECTS

Groundwater Effects

Except for gasohol, gasoline-oxygenate blends have a relatively short history, and at the present time little data are available from published literature regarding the fate and effects of these fuels in soil and groundwater. Only a few incidents of groundwater contamination by oxygenates or blends have been documented,[242-246] and little laboratory or field research has been conducted to determine the basic operative mechanisms that will control the behavior of these complex chemicals in groundwater systems. Even less information is available regarding the nature of soil contamination by these fuels.[247] Existing studies are limited in both their scope and execution and, as a result, it is not possible at this time to provide a definitive summary of the potential environmental effects of oxygenated fuels.

MTBE is slightly more soluble in water than aromatic hydrocarbons and much less soluble than alcohols.[248, 249] The percentage solubility of these substances in water is as follows:

	% Solubility
Aromatic Hydrocarbons	
Benzene	0.18
Toluene	0.05
Xylene	0.02
MTBE	4.30
Alcohols	100.00

The comparative insolubility of MTBE and aromatic hydrocarbons contrasts with the complete mutual solvency of alcohols and water. Gasoline-MTBE blends do not separate with the addition of water as do gasoline-alcohol blends as discussed in Chapter 2.

Much interest has focused on the phenomenon of cosolubility, that is, the effect of ethers or alcohols present in a gasoline-oxygenate blend on the concentration of dissolved gasoline components that are present in groundwater. Laboratory bench tests using hydrocarbon mixtures have demonstrated that the concentration of dissolved aromatics in groundwater for a gasoline-MTBE blend would not differ from the concentration encountered with gasoline.[250] However, the chemistry of cosolubility has not been fully studied in the context of blends (which are complex chemical mixtures) in the environmental settings of interest (soil and groundwater systems). What little data can be found from descriptive studies is contradictory.[243, 244] At present, there is no conclusive evidence in the literature that indicates cosolubility effects in soil and groundwater systems.

The complexity of this environmental issue will require both laboratory and field studies to provide a better understanding of the processes involved. API has initiated research activities in this area, including the environmental fate of blends in soil and groundwater, and, perhaps more importantly, on the refinement of remedial technologies that can effectively remove such contaminants from groundwater.

Clean-up strategies and goals for sites where oxygenates or blends have been released into the environment must be based on careful assessment of the environmental and health risks at the site and should focus on potential exposures to the levels of contamination that are present. When corrective action is determined to be needed at a site, clean-up can be effected using a variety of technologies that have been successfully employed for both hydrocarbon and oxygenated fuels.[242, 244, 245, 247, 251-253]

Toxicity Effects — Neat Alcohols and Ethers

METHANOL

Methanol, like ethanol, can cause central nervous system depression, but its important toxic effects in man are blindness and acidosis, which can be fatal. These effects are due to metabolism of methanol to formic acid and formate. Formic acid excess leads to acidosis, and formate has been shown to cause partial or complete blindness in monkeys.[254] Chronic exposure to high levels can also lead to blindness in humans. These effects have been manifested after ingestion, inhalation,

or dermal exposure.[255] Evidence of developmental toxicity is unclear with reported effects occurring only at very high levels.[256] A series of acute and chronic exposures have recently been conducted by the New Energy Development Organization of Japan.[257] In these experiments continuous inhalation exposure of monkeys to 3000 parts per million of methanol for 3 weeks led to slight partial atrophy of the optic nerve. Continuous exposure to 1000 parts per million for 2.5 years did not have this effect, however. Carcinogenesis studies carried out using near-continuous inhalation exposure to 1000 parts per million in rats and mice showed no increase in tumors.

ETHANOL

Chronic ethanol abuse induces liver and central nervous system toxicity.[258] Excessive consumption during pregnancy results in developmental toxicity in offspring.[259] Heavy ethanol drinkers show excessive mortality from cancers of the mouth, pharynx, larynx, esophagus, liver, and lung.[260] The acute toxicity of ethanol is low, with symptoms and death caused by narcosis.[261]

ISOPROPYL ALCOHOL (IPA)

Isopropyl alcohol (IPA) is metabolized more slowly than ethanol and is a more acutely toxic narcotizing agent.[262] Reports of adverse effects on humans are relatively few in view of the widespread use of isopropyl alcohol in industrial and chemical applications. Adverse effects have resulted from ingestion or sponge treatment for control of fever.[263, 264] Drinking-water ingestion of a high concentration of isopropyl alcohol by pregnant rats was toxic to the developing fetus.[265] Isopropyl alcohol administered by inhalation, subcutaneous injection, or skin painting for up to eight months showed no tumorigenic potential in mice.[266]

TERTIARY BUTYL ALCOHOL (TBA)

Tertiary butyl alcohol (TBA) is five times more potent than ethanol in inducing narcosis with a much longer duration. This probably is a reflection of the fact that TBA is metabolized much more slowly.[267] Irritation of the eye, nose, and throat; headache; fatigue; and dizziness are noted as symptoms of excessive exposure.[268] TBA was not mutagenic in one test system.[269]

METHYL TERTIARY BUTYL ETHER (MTBE)

Rats exposed 6 hours/day for 9 days to MTBE by inhalation demonstrated increased liver weights at 3000 parts per million and nasal and tracheal irritation at 1000 and 3000 parts per million.[270] MTBE administered by inhalation to pregnant rats was not maternally toxic, embryotoxic, or teratogenic at the highest concentration tested, 2500 parts per million.[271] A single generation, 2 litter reproduction/fertility study in rats at 250, 1000, and 2500 parts per million caused no adverse effects in the parental generation and no dose-related effects on the F_1 generations.[272] A 90-day inhalation study in rats at concentrations up to 1000 parts per million demonstrated anesthesia but no other toxicologically significant effects.[273] In vitro genetic toxicity tests were negative except for a positive result in the mouse lymphoma test system with metabolic activation and equivocal sister chromatid exchange results in Chinese hamster ovary cells.[274]

MTBE Health Effects Testing Task Force

Although MTBE does not appear to be unusually toxic in comparison with gasoline components, it clearly represents a new article of commerce on a rapid growth curve. As such it has been identified by the Federal government's Interagency Testing Commission (ITC) for listing as a candidate for further health effects testing under provisions of the Toxic Substances Control Act (TSCA). Under TSCA required testing must be supported by the producers.

In response the producers formed the MTBE Health Effects Testing Task Force (also called the MTBE Committee, affiliated with Oxygenated Fuels Association, Inc.) to negotiate a Testing Consent Order with the EPA under provisions of Section 4 of TSCA. A testing program has been developed to provide supplemental toxicological data on MTBE for EPA review and assessment, and the Task Force will now sponsor, direct, and monitor the required testing.

The MTBE Toxicology Committee, a working group of the Task Force, will address technical issues relating to the testing program. This committee will review testing guidelines and protocols, evaluate study results, prepare written comments for submittal to the EPA, and provide technical liaison with testing laboratories, consultants, monitors/auditors, and the EPA. Reporting deadlines for these studies range from 14 to 56 months.

APPENDIX A—GLOSSARY

alcohol-gasoline blend—blend of alcohol and hydrocarbons or gasoline, where the primary component is alcohol

AMC—American Motors Corporation

Antiknock Index—See (R+M)/2 Octane

API—American Petroleum Institute

ARCO—Atlantic Richfield Company

ASTM—American Society for Testing and Materials

blending value—fuel property blending value of component = { (property of mixture) - [(1 - component volume fraction) × (property of fuel before component addition)] } ÷ (component volume fraction)

Btu—British thermal unit

Bu—bushel

CBD—central business district

CMC—Changeable Methanol Concept

CO—carbon monoxide

CO_2—carbon dioxide

CRC—Coordinating Research Council

°—degree

°C—degrees Celsius

°F—degrees Fahrenheit

DDC—Detroit Diesel Corporation, formerly Detroit Diesel Allison Division of General Motors

DDGS—distillers dried grain and solubles

DOE—Department of Energy

DuPont—E. I. DuPont de Nemours and Company

EI—Evaporative Index

EPA—Environmental Protection Agency

ETBE—ethyl tertiary butyl ether

FAA—Federal Aviation Administration

FFV—flexible-fuel vehicle

FID—flame ionization detector

FTP—Federal Test Procedure

g—gram

gal—gallon, U. S.

gasohol—a mixture of one part ethanol and nine parts by volume gasoline

gasoline-oxygenate blend—a blend consisting primarily of gasoline and a substantial amount of one or more oxygenates

GM, GMR—General Motors Corporation, General Motors Research Laboratory

gpm—grams per mile; usually refers to the FTP driving cycle

GTBA—gasoline grade tertiary butyl alcohol

GTMV—Gasoline Tolerant Methanol Vehicle

HC—hydrocarbons

H_2O—water

Indolene—special gasoline formulation supplied for motor vehicle emissions certification testing

IPA—isopropyl alcohol

ITC—Interagency Testing Commission

kg—kilogram

km—kilometer

lb—pound

LPG—liquefied petroleum gas

M.A.N.—diesel engine manufacturer, formerly Maschinenfabrik Augsburg-Nuernberg Aktiengesellschaft

MBSD—thousand barrels per stream day, 330 stream days per calendar year

MBTU—thousand Btu

MM—million

MON, M—Motor octane number; see ASTM Method D 2700
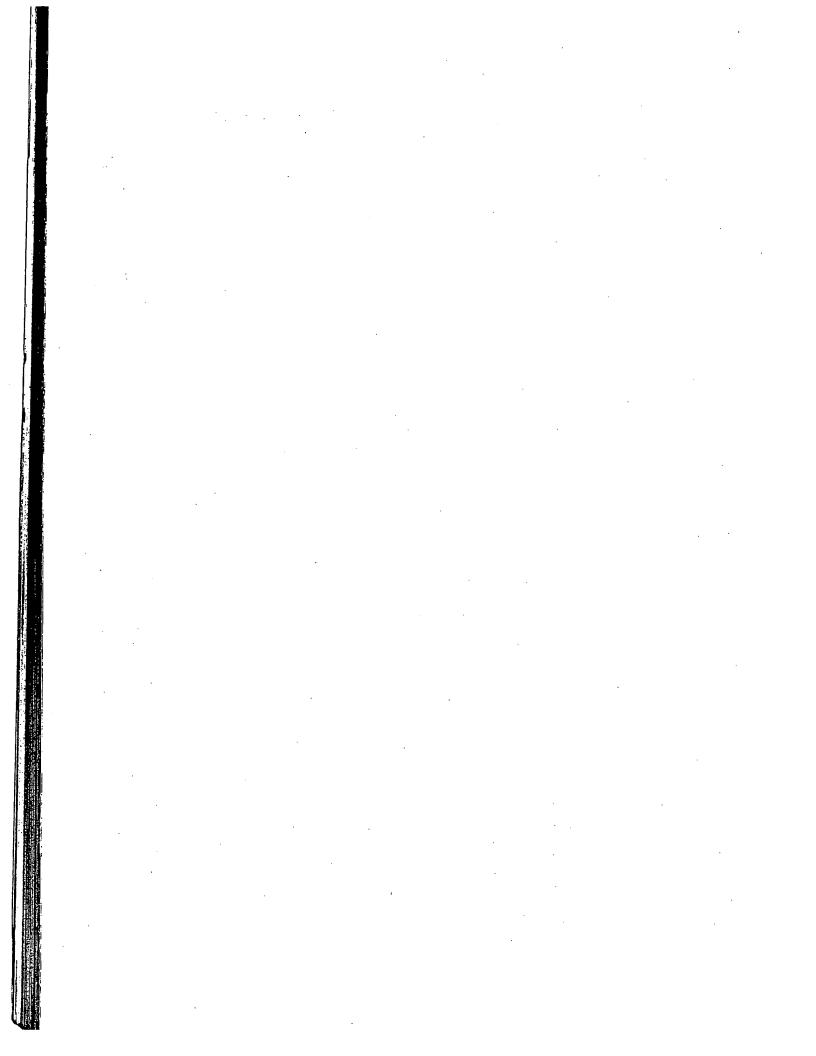
MTBE—methyl tertiary butyl ether

MVMA—Motor Vehicle Manufacturers Association

M100—100 percent methanol

M90—90 percent by volume methanol in gasoline

M85—85 percent by volume methanol in gasoline

NBR—acrylonitrile-butadiene rubber

n_D—refractive index using the sodium D line as light source; see ASTM Method D 1218

NIPER—National Institute for Petroleum and Energy Research

NO_x—oxides of nitrogen

N_2—nitrogen

OFA—Oxygenated Fuels Association

OH—hydroxyl group

oxygenate—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, that may be used as a fuel or fuel supplement

O_2—oxygen

percent evaporated—ASTM Method D 86

PFI—port fuel injection

ppm—parts per million

psi—pounds per square inch

psig—pounds per square inch gauge

(R + M)/2 Octane—average of Research and Motor octane numbers

Road Octane—octane number of fuel determined using a car on the road by CRC F-28 procedure

ROI—return on investment

RON, R—Research octane number; see ASTM Method D 2699

rpm—revolutions per minute

RVP—Reid vapor pressure; see ASTM Method D 323 modified for water sensitive fuel components

SAE—Society of Automotive Engineers

TAME—tertiary amyl methyl ether

TBA—tertiary butyl alcohol

TBI—throttle body fuel injection

TSCA—Toxic Substances Control Act

TVA—Tennessee Valley Authority

$T_{V/L=20}$—temperature at which the V/L ratio is equal to 20

VFV—Variable Fuel Vehicle

V/L—vapor-liquid ratio; see ASTM Method D 2533 modified for glycerin soluble fuel components

WOT—wide open throttle

APPENDIX B—PROPERTIES OF OXYGENATES, GASOLINE, AND NO. 2 DIESEL FUEL

Table B-1—Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Formula	CH_3OH	C_2H_5OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$	$(CH_3)_3COCH_3$	$(CH_3)_2(C_2H_5)COCH_3$	C_4 to C_{12}	C_8 to C_{25}
Molecular weight	32.04	46.07	60.09	74.12	88.15	102.18	100–105[a]	200 (approx.)
Composition, weight %								
Carbon	37.5	52.2	60.0	64.8	68.1	70.5	85–88[a]	84–87
Hydrogen	12.6	13.1	13.4	13.6	13.7	13.8	12–15[a]	13–16
Oxygen	49.9	34.7	26.6	21.6	18.2	15.7	0	0
Specific gravity, 60°F/60°F	0.796[b]	0.794[b]	0.789[b]	0.791[b]	0.744[n]	0.77[o]	0.72–0.78[a]	0.81–0.89[c]
Density, lb/gal @60°F	6.63[a]	6.61[a]	6.57[a]	6.59[a]	6.19[n]	6.41[o]	6.0–6.5[a]	6.7–7.4[c]
Boiling temperature, °F	149[b]	172[b]	180[b]	181[b]	131[b]	187[o]	80–437[a]	370–650[c]
Reid vapor pressure, psi	4.6[p]	2.3[p]	1.8[p]	1.8[p]	7.8[d]	1.5[o]	8–15[l]	<0.2
Octane no. (see note 1)								
Research octane no.	—	—	—	—	—	—	88–98[l]	—
Motor octane no.	—	—	—	—	—	—	80–88[l]	—
Cetane no. (see note 1)	—	—	—	—	—	—	—	40–55
Water solubility, @70°F								
Fuel in water, volume %	100[b]	100[b]	100[b]	100[b]	4.3[d]	—	Negligible	Negligible
Water in fuel, volume %	100[b]	100[b]	100[b]	100[b]	1.4[d]	0.6[o]	Negligible	Negligible
Freezing point, °F	-143.5[b]	-173.2[b]	-127.3[b]	78.0[b]	-164[b]	—	-40[f]	-40–30[j]
Refractive index, n_D @68°F	1.3286[b]	1.3614[b]	1.3772[b]	1.3838[b]	1.3689[b]	—	1.4–1.5[g]	1.4–1.5[g]
Viscosity								
Centipoise @68°F	0.59[k]	1.19[k]	2.38[k]	4.2 @78°F[k]	0.35[k]	—	0.37–0.44[i,q]	2.6–4.1
Centipoise @-4°F	1.15[k]	2.84[k]	9.41[k]	Solid[k]	0.60[k]	—	0.60–0.77[i,q]	9.7–17.6
Coefficient of expansion, @60°F, 1 atmosphere, per °F	0.00067[f,l]	0.00062[f,l]	—	—	0.00078[d]	—	—	0.00046
Electrical conductivity, mhos/cm	4.4×10^{-7}[h]	1.35×10^{-9}[h]	—	—	—	—	1×10^{-14}[h]	1×10^{-12}
Flash point, closed cup, °F	52[p]	55[p]	53[p]	52[p]	-14[d]	—	-45[a]	165[c]
Autoignition temperature, °F	867[a]	793[a]	750[a]	892[a]	815[d]	—	495[a]	600 (approx.)
Flammability limits, volume %								
Lower	7.3[p]	4.3[p]	2.0[p]	2.4[p]	1.6[d,f]	—	1.4[a]	1.0
Higher	36.0[p]	19.0[p]	12.0[p]	8.0[p]	8.4[d,f]	—	7.6[a]	6.0
Latent heat of vaporization								
Btu/gal @60°F	3,340[a]	2,378[a]	2,100[b]	1,700[b]	863[f]	—	900 (approx.)[a]	710 (approx.)
Btu/lb @60°F	506[a]	396[a]	320[b]	258[b]	138[f]	—	150 (approx.)[a]	100 (approx.)
Btu/lb air for stoichiometric mixture @60°F	78.4[a]	44.0[a]	31.1[b]	23.2[b]	11.8	—	10 (approx.)[a]	8 (approx.)

Table B-1—Continued

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Heating value (see note 2)								
Higher (liquid fuel–liquid water) Btu/lb								
Lower (liquid fuel–water vapor) Btu/lb	9,750[a]	12,800[a]	14,500[g]	15,500[g]	18,290[g]	—	18,800–20,400	19,200–20,000
Lower (liquid fuel–water vapor) Btu/gal @60°F	8,570[a]	11,500[a]	13,300[g]	14,280[g]	15,100[g]	15,690[o]	18,000–19,000	18,000–19,000
Gaseous fuel–water vapor Btu/lb @60°F	56,800[j]	76,000[j]	87,400[j]	94,100[j]	93,500[j]	100,600[j]	109,000–119,000	126,000–130,800
	9,080[a]	11,900[a]	—	—	—	—	19,000–19,300	—
Heating value, stoichiometric mixture								
Mixture in vapor state, Btu/cubic foot @68°F	92.5[a]	92.9[a]	—	—	—	—	95.2[a]	96.9[r,s]
Fuel in liquid state, Btu/lb of air	1,330[a]	1,280[a]	—	—	—	—	1,290[a]	—
Specific heat, Btu/lb–°F.	0.60[k]	0.57[k]	0.61[k]	0.72[k]	0.50[k]	—	0.48[f]	0.43
Stoichiometric air/fuel, weight	6.45[i]	9.00[i]	10.3[i]	11.1[i]	11.7[i]	12.1[i]	14.7[i]	14.7
Volume % fuel in vaporized stoichiometric mixture	12.3[a]	6.5[a]	—	—	2.7[f]	—	2.0[a]	—
Ratio moles product/moles charge	1.06[i]	1.07[i]	1.07[i]	1.07[i]	1.07[i]	1.07[i]	1.05[i,m]	1.06[i,r]
Ratio moles product/moles $O_2 + N_2$	1.21[i]	1.12[i]	1.10[i]	1.10[i]	1.10[i]	1.09[i]	1.08[i,m]	1.07[i,r]

Notes:

1. Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with hydrocarbons. Similar problems exist for cetane rating procedures.

2. The higher heating value is cited for completeness only. Since no vehicles in use, or currently being developed for future use, have powerplants capable of condensing the moisture of combustion, the lower heating value should be used for practical comparisons between fuels.

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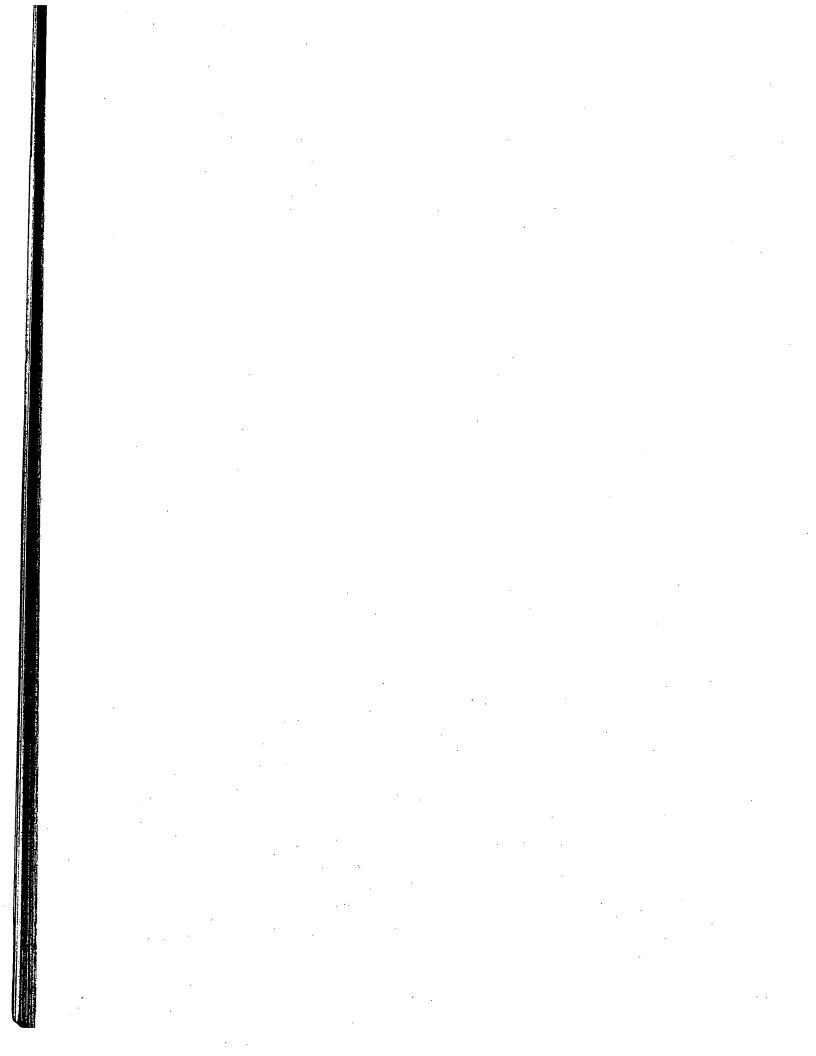
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Order No. 822-42610

American Petroleum Institute
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Washington, D.C. 20005

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Applicant:	§	
	§	Group Art Unit: 1714
CHARLES A. LIEDER	§	
LLOYD E. FUNK	§	Examiner: Cephia D. Toomer
DAVID A. BARKER	§	
	§	
Filed: April 21, 2000	§	
	§	
Serial No.: 09/556,852	§	
	§	
For: GASOLINE-OXYGENATE BLEND	§	
AND METHOD OF PRODUCING	§	
THE SAME	§	Attorney Docket No.: 013129/00025

DECLARATION OF CHARLES A. LIEDER, Ph.D., UNDER 37 C.F.R. 1.132

I Charles A. Lieder do hereby state:

1.   I am over the age of 18;

2.   I received a Ph.D. degree in Physical Chemistry from Stanford University in 1974. I further received a B.A. degree in Chemistry and Math from Hope College in 1970.

3.   I have been employed by Shell Oil Company ("Shell") since 1974. My first position at Shell was as a Research Scientist in Reaction/Environmental Engineering. Since that time, I have served as a Supervisor for Process Development, Technical Manager in Process Engineering, an Operations Manager in Crude/Diesel/Hydrogen/Sulfur, a Senior Staff Engineer to Fuels Regulatory Technical Support and an Engineering Advisor in Gasoline/Fuels Blending Technology. From 1989 to 1990, I was an "Executive-on-Loan" to the California Energy Commission.

4.   I am a co-inventor of the above-referenced patent application and am familiar with the claims as presently pending before the U.S. Patent and Trademark Office. I am also familiar with the claims as amended and the new claims added to this application, as set forth in the contemporaneously filed Amendment and Response to Office Action of 10 September 2004. All of the presently pending claims are directed to a blend of a gasoline and an oxygenate wherein the Dry Vapor Pressure Equivalent is less than about 7.2 PSI.

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5.   I have read and reviewed U.S. Patent No. 5,679,117 ("*Jarvis*"). *Jarvis* discloses a "final liquid product 60" prepared by subjecting a mixture of ethanol and butane or natural gasoline to processing conditions in the presence of a platinum catalyst. (Line 25 of column 4 through line 24 of column 5.)

6.   The Table in column 5 of *Jarvis* indicates that the amount of n-butane in the "final liquid product 60" is 53.03 volume percent and the amount of ethanol is 42.75 volume percent. The "final liquid product 60" of the Table is a blend of 53.03 volume percent of n-butane and 42.75 volume percent of ethanol. The minimum RVP of "final liquid product 60" is approximately 37.16:

Component	Known RVP of Component	Approx. Mole Fraction	RVP x Approx. Mole Fraction
n-butane	54	0.53	28.62
Ethanol	18	0.43	7.74
Pentanes	20	0.04	0.80

Total: 37.16 = RVP of Mixture

7.   *Jarvis* discloses in lines 25-28 of column 5 that a high-octane gasoline may be prepared by adding 20% by volume of final liquid product 60 to 80 octane gasoline to render a resulting mixture having 92.8 octane "with a vapor pressure in the range of 4 to 19 pounds per square inch." The theoretical RVP of 20% by volume of "the new product" would, at best, be 7.4 (0.20 x 37.16). A high-octane gasoline having a vapor pressure between 4 to 7.4, based on this disclosure in *Jarvis*, is scientifically impossible.

8.   In lines 65-67 of column 5 of *Jarvis*, the patentees provide an example wherein the resulting product is "substantially one half natural gasoline and one half ethanol". The RVP of such a product would be outside of the claimed ranges of the present application. The blending RVP of ethanol is 18.0. The natural gasoline, as described in lines 49-64, contains 53.871% by liquid volume C6+, 3.03% by liquid volume butane, 0.697% liquid volume neo-pentane, 26.046% by liquid volume iso-pentane and 16.349% by liquid volume normal pentane. The (approximate) calculated RVP of the natural gasoline is as follows:

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Component	Known RVP of Component	Approx. Mole Fraction	RVP x Approx. Mole Fraction
C6+	11	0.539	5.93
Butane	54	0.03	1.62
Neo-pentane	31	0.007	0.22
Iso-pentane	19	0.26	4.94
n-pentane	16	0.163	2.61

Total: 15.32psi =RVP of Mixture

The theoretical RVP for the product containing one half of such natural gasoline and one half of ethanol would therefore be 16.66 PSI:

Component	Known RVP of Component	Approx. Mole Fraction	RVP x Approx. Mole Fraction
Gasoline	15.3	0.50	7.66
Ethanol	18	0.50	9.0

Total: 16.66psi = RVP of Mixture

The statement in lines 65-67 of *Jarvis* that the resulting product has a vapor pressure between 1.5 and 8.0 psi is incorrect. A blend of 50% ethanol and 50% of the stated gasoline formulation could not render a product having a vapor pressure less than 16.66 PSI.

9.   Lines 27-28 of column 6 of *Jarvis* describes a "pump gasoline" wherein the "final product has a vapor pressure in the range from 6 to 8 psi which is an acceptable range." "Pump gasoline" is defined in *Jarvis* as a high-octane gasoline (line 11 of column 1). Specifications for high-octane gasoline for use as pump gasoline in service stations available to the U.S. public, for the time period February 8, 1995 to October 21, 1996[1], are set forth in ASTM D 4814-95c, "Standard Specification for Automotive Spark-Ignition Engine Fuel", copy attached as *Exhibit A*. It is unclear as to whether "final product" in line 26 of *Jarvis* refers to "final liquid product 60" or a high-octane. I would infer, however, that "final product" refers to a high-octane gasoline since *Jarvis* concludes that the "final product is pump gasoline" (line 26 of column 6). However, an admixture of "final liquid product 60" and a hydrocarbon stream could not render a "pump gasoline" having a vapor pressure in the range from 6 to 8 psi in accordance with the standards set forth in ASTM D 4814-95c.

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[1] *Jarvis* matured from U.S. Patent Application Serial No. 734,091, filed on October 21, 1996; the parent application to U.S. Patent Application Serial No. 734,091 was filed on February 8, 1995.

As set forth in paragraph 6 above, "Final liquid product 60" has a calculated RVP of 37.16 psi. In order to comply with the maximum ethanol concentration of 10 volume percent as set forth by the EPA in Table 11 on page 24 of API Publication, Second Edition, July 1988, attached to the Amendment filed on August 24, 2001, only about 20 volume percent of "Final liquid product 60" could be used in admixture with a second hydrocarbon stream. As set forth in paragraph 7 above, 20% by volume of "Final liquid product 60" would have a RVP of 7.4 psi and 10 volume percent ethanol (49.94 x 0.20). In order for the RVP of the "final product" to be less than 8 psi (the "final liquid product 60" having a RVP of 7.4 psi), the remaining 80 volume percent of the other hydrocarbon stream would have to have a RVP < 0.6 psi. The hydrocarbon stream to meet this objective would likely be jet fuel or jet fuel constituents, such as a C_9-C_{11} hydrocarbon stream containing nonane, decane and/or hendane.

Even in such instances, while the RVP would be < 8psi; the mid-distillation point (T-50) of the "final product" would violate the standards set forth in D 4814 95c. The T-50 set forth in D 4814 95c must be less than 250° F, and the T-50 of the "final product" would be greater than 300° F. The resulting "final product" could therefore not be considered a "pump gasoline".

Further, the "final product" would be considered a "gap" fuel because it contains two different components (high volatility and low volatility) and thus lacks molecules in the mid-range distillation region. Gap fuels have poor startup and enhanced stalling characteristics. These characteristics defined the driveability of gasoline. The "final product" of lines 20-28 of column 6 of *Jarvis* would not pass the driveability recommendations of D 4814 95c or the internal specifications of common carrier pipelines in the U.S.

It can therefore be concluded that even if the "final product", referenced in lines 27-28 of column 6 of *Jarvis*, had a Dry Vapor Pressure Equivalent less than 7.2 PSI, the admixture could not be classified as a "pump gasoline".

The conclusions expressed in this paragraph would be the same using the current specifications for "Pump Gasoline" for use in the United States, as set forth in ASTM D 4814-04a, "Standard Specification for Automotive Spark-Ignition Engine Fuel", copy attached as *Exhibit B*.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and believe are believe to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are

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punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

DATED: December 13, 2004

Charles A. Lieder

Charles A. Lieder, Ph.D.

5

Standard Specification for
Automotive Spark-Ignition Engine Fuel[1]

This standard is issued under the fixed designation D 4814; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This specification guides in establishing requirements of automotive fuels for ground vehicles equipped with spark-ignition engines.

1.2 This specification describes various characteristics of automotive fuels for use over a wide range of operating conditions. It provides for a variation of the volatility and water tolerance of automotive fuel in accordance with seasonal climatic changes at the locality where the fuel is used. For the period May 1 through September 15, the maximum vapor pressure limits issued by the U.S. Environmental Protection Agency (EPA) are specified for each geographical area except Alaska and Hawaii. Variation of antiknock index with seasonal climatic changes and altitude is discussed in Appendix X1. This specification neither necessarily includes all types of fuels that are satisfactory for automotive vehicles, nor necessarily excludes fuels that can perform unsatisfactorily under certain operating conditions or in certain equipment. The significance of each of the properties of this specification is shown in Appendix X1.

1.3 The spark-ignition engine fuels covered in this specification are gasoline and its blends with oxygenates such as alcohols and ethers. This specification does not apply to fuels that contain an oxygenate as the primary component, such as Fuel Methanol (M85). The concentrations and types of oxygenates are not specifically limited in this specification. However, depending on oxygenate type, as oxygenate content increases above some threshold level, the likelihood for vehicle problems also increases. The composition of both unleaded and leaded fuel is limited by economic, legal, and technical consideration, but their properties, including volatility, are defined by this specification. In addition, the composition of unleaded fuel is subject to the rules, regulations, and Clean Air Act waivers of the U.S. Environmental Protection Agency (EPA). With regard to fuel properties, including volatility, this specification can be more or less restrictive than the EPA rules, regulations, and waivers. Refer to Appendix X3 for discussions of EPA rules relating to fuel volatility, lead and phosphorous contents, and use of oxygenates in blends with unleaded gasoline. Contact EPA for the latest versions of the rules and additional requirements.

1.4 This specification does not address the emission characteristics of reformulated spark-ignition engine fuel. Reformulated spark-ignition engine fuel is required in some areas to lower emissions from automotive vehicles, and its characteristics are described in the research report on reformulated spark-ignition engine fuel.[2] However, in addition to the legal requirements found in this research report, reformulated spark-ignition engine fuel should meet the performance requirements found in this specification.

1.5 This specification represents a description of automotive fuel as of the date of publication. The specification is under continuous review, which can result in revisions based on changes in fuel, automotive requirements, or test methods, or a combination thereof. All users of this specification, therefore, should refer to the latest edition.

NOTE 1—If there is any doubt as to the latest edition of Specification D 4814, contact ASTM Headquarters.

1.6 Tests applicable to gasoline are not necessarily applicable to its blends with oxygenates. Consequently, the type of fuel under consideration must first be identified in order to select applicable tests. Test Method D 4815 provides a procedure for determining oxygenate concentration in mass percent. Test Method D 4815 also includes procedures for calculating mass oxygen content and oxygenate concentration in volume percent. Appendix X4 provides a procedure for calculating the mass oxygen content of a fuel using measured oxygenate type, oxygenate concentration in volume percent, and measured density or relative density of the fuel.

1.7 The test method in Annex A1 is state-of-the-art; however, it may be revised and eventually balloted for publication as a separate standard.

1.8 The values stated in SI units are the standard, except when other units are specified by federal regulation. Values given in parentheses are provided for information only.

NOTE 2—Many of the values shown in Table 1 were originally developed using U.S. customary units and were subsequently soft-converted to SI values. As a result, conversion of the SI values will sometimes differ slightly from the U.S. customary values shown because of round-off. In some cases, federal regulations specify non-SI units.

1.9 The following safety hazard caveat pertains only to the test method portion, Annex A1 of this specification. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

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[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A on Gasoline and Oxygenated Fuels.

Current edition approved Dec. 10, 1995. Published February 1996. Originally published as D 4814 – 88. Last previous edition D 4814 – 95b.

[2] Available from ASTM Headquarters. Request RR:D02-1347.

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D 4814

2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products[3]

D 130 Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test[3]

D 287 Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)[3]

D 381 Test Method for Existent Gum in Fuels by Jet Evaporation[3]

D 439 Specification for Automotive Gasoline[4]

D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)[3]

D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)[3]

D 1298 Test Method for Density, Relative Density (Specific Gravity) or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[3]

D 2500 Test Method for Cloud Point of Petroleum Oils[3]

D 2533 Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels[3]

D 2622 Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry[5]

D 2699 Test Method for Knock Characteristics of Motor Fuels by the Research Method[6]

D 2700 Test Method for Knock Characteristics of Motor and Aviation Fuels by the Motor Method[6]

D 2885 Test Method for Research and Motor Method Octane Ratings Using On-Line Analyzers[6]

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[5]

D 3231 Test Method for Phosphorus in Gasoline[5]

D 3237 Test Method for Lead in Gasoline by Atomic Absorption Spectrometry[5]

D 3341 Test Method for Lead in Gasoline—Iodine Monochloride Method[5]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[5]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[5]

D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination[5]

D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary–Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography[7]

D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)[7]

D 5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy[7]

D 5188 Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)[7]

D 5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method)[7]

D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)[7]

D 5453 Test Method for the Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Ultraviolet Fluorescence[7]

D 5482 Test Method for Vapor Pressure of Petroleum Products (Mini Method-Atmospheric)[7]

E 1 Specification for ASTM Thermometers[8]

3. Terminology

3.1 *Definitions:*

3.1.1 *antiknock index, n*—the arithmetic average of the Research octane number (RON) and Motor octane number (MON), that is, (RON + MON)/2.

3.1.2 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

3.1.3 *gasoline-alcohol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass percent oxygen, or more than 0.15 mass percent oxygen if methanol is the only oxygenate) of one or more alcohols.

3.1.4 *gasoline-ether blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass percent oxygen) of one or more ethers.

3.1.5 *gasoline-oxygenate blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass percent oxygen, or more than 0.15 mass percent oxygen if methanol is the only oxygenate) of one or more oxygenates.

3.1.6 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which can be used as a fuel or fuel supplement.

3.2 *Applicability*—In order to determine when a fuel contains a substantial amount of an oxygenate, a gasoline-oxygenate blend is defined as a fuel which contains more than 0.35 mass percent oxygen, or more than 0.15 mass percent oxygen if methanol is the only oxygenate. The definitions in this section do not apply to fuels that contain an oxygenate as the primary component; for example, fuel methanol (M85).

NOTE 3—The criteria in 3.2 were selected with consideration given to current oxygenate levels in the marketplace, state labeling practices, and consistency with federal legislation and regulations.

NOTE 4—Refer to Test Method D 4815 to calculate the mass oxygen content of a fuel using oxygenate concentration in mass percent. Refer to Appendix X4 to calculate mass oxygen content of a fuel using oxygenate concentration in volume percent.

4. Ordering Information

4.1 The purchasing agency shall:

4.1.1 State the antiknock index as agreed upon with the seller,

4.1.2 Indicate the season and locality in which the fuel is to be used,

4.1.3 Indicate the lead level required (Table 3), and

4.1.4 State the concentration and types of oxygenates present as agreed upon with the seller.

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[3] *Annual Book of ASTM Standards,* Vol 05.01.
[4] Discontinued—See 1990 *Annual Book of ASTM Standards,* Vol 05.01.
[5] *Annual Book of ASTM Standards,* Vol 05.02.
[6] *Annual Book of ASTM Standards,* Vol 05.04.
[7] *Annual Book of ASTM Standards,* Vol 05.03.

[8] *Annual Book of ASTM Standards,* Vol 14.03.

TABLE 1 Vapor Pressure and Distillation Class Requirements

Vapor Pressure/ Distillation Class	Vapor Pressure,[A] max, kPa(psi)	Distillation Temperatures, °C(°F), at % Evaporated[B]					Distillation Residue, vol %, max
		10 vol %, max	50 vol %		90 vol %, max	End Point, max	
			min	max			
AA	54(7.8)	70(158)	77(170)	121(250)	190(374)	225(437)	2
A	62(9.0)	70(158)	77(170)	121(250)	190(374)	225(437)	2
B	69(10.0)	65(149)	77(170)	118(245)	190(374)	225(437)	2
C	79(11.5)	60(140)	77(170)	116(240)	185(365)	225(437)	2
D	93(13.5)	55(131)	66(150)	113(235)	185(365)	225(437)	2
E	103(15.0)	50(122)	66(150)	110(230)	185(365)	225(437)	2

[A] Consult EPA for approved test methods for compliance with EPA vapor pressure regulations.
[B] At 101.3 kPa pressure (760 mm Hg).

TABLE 2 Vapor Lock Protection Class Requirements

Vapor Lock Protection Class	Vapor/Liquid Ratio (V/L)[A,B]	
	Test Temperature, °C(°F)	V/L, max
1	60(140)	20
2	56(133)	20
3	51(124)	20
4	47(116)	20
5	41(105)	20

[A] At 101.3 kPa pressure (760 mm Hg).
[B] The mercury confining fluid procedure of Test Method D 2533 shall be used for gasoline-oxygenate blends. Either glycerin or mercury confining fluid may be used for gasoline. Test Method D 5188 may be used for all fuels. The procedure for estimating temperature-V/L (see Appendix X2) may only be used for gasoline.

5. Performance Requirements

5.1 Some requirements and test methods applicable to automotive spark-ignition engine fuel depend on whether the fuel is a gasoline, or a gasoline-oxygenate blend. Test Method D 4815, a gas chromatographic test method, is the recommended procedure to detect the types and amounts of oxygenates. Once the type of fuel is known, the appropriate requirements and test methods can be identified by reference to Tables 1 and 2 and Section 7.

5.2 Volatility of fuels is varied for seasonal climatic changes and conformance to U.S. EPA volatility regulations by providing six vapor pressure/distillation classes and five vapor lock protection classes for fuel. Volatility of fuel is specified by an alphanumeric designation that uses a letter from Table 1 and a number from Table 2.

5.2.1 The seasonal and geographic distribution of the combined vapor pressure/distillation-vapor lock classes is shown in Table 4.

5.2.2 The EPA vapor pressure regulations can cause the distillation of the fuel to be less volatile, which for some vehicles, results in poorer warmup driveability performance.

5.2.3 Test Method D 2533 contains procedures for measuring temperature-V/L of both gasoline and gasoline-oxygenate blends. For gasoline-oxygenate blends, the procedure requires that mercury be used as the confining fluid in place of glycerin. Either confining fluid may be used for gasoline. Test Method D 5188 is an alternative method for determining vapor-liquid ratio temperatures by an evacuated chamber method for gasoline-oxygenate blends, as well as gasoline. In case of dispute, Test Method D 2533 is the referee method. The method for estimating temperature-V/L (see Appendix X2) is only applicable for gasoline.

5.3 Antiknock index (AKI) is very important to engine performance. The matching of engine octane requirement to fuel octane level (AKI) is critical to the durability and

performance of engines; this cannot be accomplished with a single specified minimum level of antiknock index. Appendix X1 includes a discussion of antiknock indexes of fuels currently marketed and relates these levels to the octane needs of broad groups of engines and vehicles. Also discussed is the effect of altitude and weather on vehicle antiknock requirements.

5.4 Additional fuel requirements are shown in Table 3.

5.5 The properties of gasoline-oxygenate blends can differ considerably from those of gasoline. Consequently, additional requirements are needed for gasoline-oxygenate blends. These requirements involve evaluation of compatibility with plastic and elastomeric materials in fuel systems, corrosion of metals, and especially in the case of gasoline-alcohol blends, water tolerance. Requirements for metal corrosion (other than copper) and material compatibility are not given because test methods and appropriate limits are still under development. When these have been developed they will be included in this specification. Water tolerance is specified in Table 5.

5.6 Depending on oxygenate type and concentration in the blend, vehicle driveability with gasoline-oxygenate blends can differ significantly from that with gasolines having similar volatility characteristics.

5.7 *Water Tolerance:*

5.7.1 The term water tolerance is used to indicate the ability of a gasoline-oxygenate blend to dissolve water without phase separation. This may not be a problem with gasoline-ether blends, but it is of primary concern for alcohol-containing blends, as blends of gasoline with low-molecular weight alcohols generally will dissolve about 0.1 to 0.7 mass % of water under normal conditions, depending on the nature and amount of the alcohol(s) used, the specific hydrocarbons present, and the temperature of the blend. When blends are exposed to a greater amount of water than they can dissolve, they separate into an alcohol-rich aqueous phase, the volume of which can be significantly greater than that of the additional water, and an alcohol-poor hydrocarbon phase. As the aqueous phase can be highly corrosive to many metals and the engine cannot operate on it, such separation is very undesirable. Blends containing low-molecular weight alcohols are generally hygroscopic and can eventually absorb enough moisture from ambient air to cause separation. The problem of phase separation can usually be avoided if the fuels are sufficiently water-free initially and care is taken during distribution to prevent contact with water. To help ensure this, gasoline-oxygenate blends shall be tested at the lowest temperatures to which they can be subjected, dependent on the time and place of intended use, as indicated in Table 5. The values in Table 5

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TABLE 3 Detailed Requirements for all Volatility Classes[A]

Lead Content, max, g/L (g/U.S. gal)[B]		Copper Strip Corrosion, max	Solvent-washed Gum Content, mg/100 mL	Sulfur, max, mass %		Oxidation Stability, Minimum, minutes	Water Tolerance
Unleaded	Leaded			Unleaded	Leaded		
0.013(0.05)	1.1(4.2)	No. 1	5	0.10	0.15	240	C

[A] See Appendix X1 for information on Antiknock Index.

[B] See Appendix X3 for U.S. EPA maximum limits for lead and phosphorus contents in unleaded gasoline (X3.2.1) and maximum average lead limits for leaded gasoline (X3.2.2).

[C] Water tolerance limits in terms of maximum temperature for phase separation are given in Table 5 (consult Annex A1).

are the 10th percentile 6-h minimum temperatures, with each reading specifically defined as the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. For April through September (and occasionally October, and year-round for Hawaii), Table 5 specifies a minimum phase separation temperature of 10°C (50°F), even though the 10th percentile 6-h minimum temperature can be higher. Use of this temperature limit also reduces the risk of separation of the fuel in storage tanks where temperatures may be lower than ambient.

NOTE 5—The values in Table 5 are taken from the U.S. Army Belvoir Research Development and Engineering Center's Report No. 316, entitled "A Predictive Study for Defining Limiting Temperatures and Their Application in Petroleum Product Specifications." This can be obtained as Publication AD756-420 from the National Technical Information Service, Springfield, VA 22151.

5.7.2 The test procedure (see Annex A1) consists of cooling the fuel under specified conditions to the appropriate temperature listed in Table 5. It is important to note that when cooling to a low temperature some gasolines and many gasoline-oxygenate blends, especially those containing ethers, can take on a hazy appearance. This haze must be carefully distinguished from the test criterion described in Annex A1 of separation into two distinct phases with a more or less distinct common boundary, and must not be considered grounds for rejection of the fuel. This test also must not be confused with that described in Section 6, which is conducted at 21°C (70°F) or above, and for which the appearance of haze is proper grounds for rejection.

6. Workmanship

6.1 The finished fuel shall be visually free of undissolved water, sediment, and suspended matter; it shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

6.2 Fuel to be used in this test shall not be cooled below about 15°C (59°F) or its temperature at the time the sample was taken, whichever is lower, as cooling of gasoline-oxygenate blends can produce changes in appearance that are not reversed on rewarming.

7. Test Methods

7.1 The requirements of this specification shall be determined in accordance with the methods listed below. Refer to the listed test methods to determine applicability or required modifications for use with gasoline-oxygenate blends.

7.1.1 *Distillation*—Test Method D 86.

7.1.2 *Vapor-Liquid Ratio*—Test Method D 2533 has procedures for determining vapor-liquid (V/L) ratios for both gasoline and gasoline-oxygenate blends. Because some oxygenates are miscible with the glycerin used in one procedure, another procedure using mercury as the confining fluid is

provided for gasoline-oxygenate blends. Either procedure may be used to determine V/L for gasoline. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. It may be used for gasoline and gasoline-oxygenate blends.

7.1.3 *Vapor Pressure*—Test Methods D 4953, D 5190, D 5191, or D 5482.

7.1.4 *Corrosion, for Copper*, Test Method D 130, 3 h at 50°C (122°F).

7.1.5 *Solvent-Washed Gum Content*—Test Method D 381, air jet apparatus.

7.1.6 *Sulfur*—Test Methods D 1266, D 2622, D 3120, or D 5453. With Test Method D 3120, fuels with sulfur content greater than 100 ppm (0.0100 mass %) must be diluted with *isooctane*. The dilution of the sample may result in a loss of precision. Test Method D 3120 cannot be used when the lead concentration is greater than 0.4 g/L (1.4 g/U.S. gal).

7.1.7 *Lead*—Test Methods D 3341 or D 5059 (Test Methods A or B). For lead levels below 0.03 g/L (0.1 g/U.S. gal) use Test Methods D 3237 or D 5059 (Test Method C).

7.1.8 *Oxidation Stability*—Test Method D 525.

7.1.9 *Oxygenate Detection*—Test Method D 4815 is designed for the quantitative determination of methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropylether, methyl alcohol, ethyl alcohol, isopropyl alcohol, *n*-propyl alcohol, isobutyl alcohol, *tert*-butyl alcohol, sec-butyl alcohol, *n*-butyl alcohol, and *tert*-amyl alcohol. Results are reported in mass percent, but Test Method D 4815 includes procedures for calculating oxygenate concentration in volume percent and mass oxygen content using mass percent oxygenate results.

7.1.10 *Water Tolerance*—See Annex A1 for a test method.

8. Precision and Bias •

8.1 The precision of each required test method with gasoline is included in the standard applicable to each method. In many cases, the precision applicable to gasoline-oxygenate blends has not been established yet.

9. Keywords

9.1 alcohol; antiknock index; automotive fuel; automotive gasoline; automotive spark-ignition engine fuel; copper strip corrosion; corrosion; distillation; driveability; EPA regulations; ethanol; ether; fuel; gasoline; gasoline-alcohol blend; gasoline-ethanol blend; gasoline- ether blend; gasoline-oxygenate blend; induction period; lead; leaded fuel; methanol; MTBE; octane number; octane requirement; oxidation stability; oxygenate; oxygenate detection; phase separation; phosphorous; solvent-washed gum; sulfur; $T_{V/L}$ = 20; unleaded fuel; vapor-liquid ratio; vapor lock; vapor pressure; volatility; water tolerance

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TABLE 4 Schedule of Seasonal and Geographical Volatility Classes[A]

This schedule, subject to agreement between purchaser and seller, denotes the volatility properties of the fuel at the time and place of bulk delivery to the fuel dispensing facilities for the end user. For Sept. 16 through April 30 (the time period not covered by EPA Phase II vapor pressure requirements), volatility properties for the previous month or the current month are acceptable for the end user from the 1st through the 15th day of the month. From the 16th day through the end of the month, volatility properties of the fuel delivered to the end user shall meet the requirements of the specified class(es). To ensure compliance with EPA Phase II vapor pressure requirements, vapor pressure for finished gasoline tankage at refineries, importers, pipelines, and terminals during May and for the entire distribution system, including retail stations, from June 1 to Sept. 15 shall meet only the current month's class. Shipments should anticipate this schedule.

Where alternative classes are listed, either class or intermediate classes are acceptable; the option shall be exercised by the seller.

State	Jan.	Feb.	Mar.	Apr.	May[B]	June	July	Aug.	Sept. 1-15	Sept. 16-30	Oct.	Nov.	Dec.
Alabama	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-2[E]	A-2[E]	A-2/C-3	C-3	C-3/D-4	D-4
Alaska	E-5	E-5	E-5	E-5	E-5/D-4	D-4	D-4	D-4	D-4	D-4/E-5	E-5	E-5	E-5
Arizona													
N 34° Latitude and E 111° Longitude	D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-1	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Remainder of State	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F]	A-1[F]	A-1[E]	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Arkansas	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
California:													
North Coast	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[D]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
South Coast	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[E]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Southeast	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F]	A-1[F]	A-1[F]	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Interior	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[E]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Colorado	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[E]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Connecticut	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Delaware	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
District of Columbia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-3[D]	A-3[D]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Florida	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-3[D]	A-3[D]	A-3/C-3	C-3	C-3/D-4	D-4
Georgia	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-2[E]	A-2[E]	A-2/C-3	C-3	C-3/D-4	D-4
Hawaii	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3
Idaho:													
N 46° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
S 46° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Illinois:													
N 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
S 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4	D-4/E-5
Indiana	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Iowa	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Kansas	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[E]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Kentucky	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Louisiana	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-2[E]	A-2[E]	A-2/C-3	C-3	C-3/D-4	D-4
Maine	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Maryland	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[D]	A-3[D]	A-3[D]	A-3[D]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Massachusetts	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Michigan	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Minnesota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Mississippi	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-3	A-2	A-2	A-2/C-3	C-3	C-3/D-4	D-4
Missouri	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[D]	A-2[E]	A-2[E]	A-2[E]	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Montana	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Nebraska	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Nevada:													
N 38° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[E]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
S 38° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4
New Hampshire	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
New Jersey	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
New Mexico:													
N 34° Latitude	E-5/D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
S 34° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4	D-4
New York	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
North Carolina	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-2[E]	A-2[E]	A-2/C-3	C-3/D-4	D-4	D-4/E-5
North Dakota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Ohio	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Oklahoma	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Oregon:													
E 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
W 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3[D]	A-3[D]	A-3[D]	A-3[D]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Pennsylvania	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Rhode Island	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
South Carolina	D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4
South Dakota	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Tennessee	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-2[E]	A-2[E]	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Texas:													
E 99° Longitude	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[D]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4
W 99° Longitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F]	A-1[F]	A-1[F]	A-1/B-2	B-2/C-3	C-3/D-4	D-4
Utah	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[E]	A-2[E]	A-2[E]	A-2[E]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Vermont	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Virginia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[D]	A-3[D]	A-3[D]	A-3[D]	A-3/C-3	C-3/D-4	D-4/E-5	E-5

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TABLE 4 (Continued)

State	Jan.	Feb.	Mar.	Apr.	May[B]	June	July	Aug.	Sept. 1–15	Sept. 16–30	Oct.	Nov.	Dec.
Washington:													
E 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
W 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
West Virginia	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wisconsin	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wyoming	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5

[A] For the period May 1 through September 15, the specified vapor pressure classes comply with 1992 U.S. EPA Phase II volatility regulations. EPA regulations allow 1.0 psi higher vapor pressure for gasoline-ethanol blends containing 9 to 10 vol % ethanol for the same period. See Appendix X3 for additional federal volatility regulations.

[B] Values in parentheses are permitted for retail stations and other end users.

[C] Details of State Climatological Division by county as indicated:

California, North Coast—Alameda, Contra Costa, Del Norte, Humbolt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity

California, Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (except that portion lying east of Los Angeles County Aqueduct), Kings, Madera, Mariposa, Merced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada

California, South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct)

California, Southeast—Imperial, Riverside, San Bernadino, Los Angeles (that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct)

[D] AA-3 for the following ozone nonattainment areas:
(See Federal Register 56, 215, 56694, November 6, 1991, for description of the geographic boundary for each area.)

Alabama—Birmingham
California—Monterey Bay
California—San Francisco-Bay Area
District of Columbia—Washington
Florida—Jacksonville
Florida—Miami-Fort Lauderdale-West Palm Beach
Florida—Tampa-St. Petersburg-Clearwater
Georgia—Atlanta
Louisiana—Baton Rouge
Louisiana—Beauregard Parish
Louisiana—Grant Parish
Louisiana—Lafayette
Louisiana—Lafourche Parish
Louisiana—Lake Charles
Louisiana—New Orleans
Louisiana—St. James Parish
Louisiana—St. Mary Parish
Maryland—Baltimore
Maryland—Kent and Queen Anne's Counties
Maryland—Philadelphia-Wilmington-Trenton Area

Maryland—Washington Area
Missouri—Kansas City
Missouri—St. Louis
North Carolina—Charlotte-Gastonia
North Carolina—Greensboro-Winston Salem-High Point
North Carolina—Raleigh-Durham
Oregon—Portland-Vancouver AQMA
Oregon—Salem
Tennessee—Memphis
Tennessee—Nashville
Texas—Beaumont-Port Arthur
Texas—Dallas-Fort Worth
Texas—Houston-Galveston-Brazoria
Texas—Victoria
Virginia-Norfolk-Virginia Beach-Newport News
Virginia—Richmond
Virginia—Smyth County
Virginia—Washington Area

[E] AA-2 for the following ozone nonattainment areas:
(See Federal Register 56, 215, 56694, November 6, 1991, for description of the geographic boundary for each area.)

Alabama—Birmingham
Arizona—Phoenix
California—Chico
California—Los Angeles-South Coast Air Basin
California—Monterey Bay
California—Sacramento Metro
California—San Diego
California—San Francisco-Bay Area
California—San Joaquin Valley
California—Santa Barbara-Santa Maria-Lompoc
California—Ventura County
California—Yuba City
Colorado—Denver-Boulder
Georgia—Atlanta
Kansas—Kansas City
Louisiana—Baton Rouge
Louisiana—Beauregard Parish
Louisiana—Grant Parish
Louisiana—Lafayette
Louisiana—Lafourche Parish

Louisiana—Lake Charles
Louisiana—New Orleans
Louisiana—St. James Parish
Louisiana—St. Mary Parish
Missouri—Kansas City
Missouri—St. Louis
Nevada—Reno
North Carolina—Charlotte-Gastonia
North Carolina—Greensboro-Winston Salem-High Point
North Carolina—Raleigh-Durham
Tennessee—Memphis
Tennessee—Nashville
Texas—Beaumont-Port Arthur
Texas—Dallas-Forth Worth
Texas—Houston-Galveston-Brazoria
Texas—Victoria
Utah—Salt Lake City

[F] AA-1 for the following ozone nonattainment areas:
(See Federal Register 56, 215, 56694, November 6, 1991, for description of the geographic boundary for each area.)

Arizona—Phoenix
California—Imperial County
California—Southeast Desert Modified AQMA
Texas—El Paso

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TABLE 5 Maximum Temperature for Phase Separation, °C[A]

State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
					Temperature Conversion °F = (°C × 1.8) + 32°							
Alabama	−4	−3	0	5	10	10	10	10	10	6	0	−4
[B]Alaska:												
Southern Region	−27	−26	−23	−11	1	7	9	7	1	−9	−19	−23
South Mainland	−41	−39	−31	−14	−1	7	9	5	−2	−18	−32	−41
N of 62° Latitude												
Arizona:												
N of 34° Latitude	−11	−7	−7	−2	2	6	10	10	6	1	−6	−9
S of 34° Latitude	−2	−1	2	7	10	10	10	10	10	9	2	−1
Arkansas	−8	−6	−2	6	10	10	10	10	10	4	−2	−6
[C] California												
North Coast	−2	0	1	4	5	8	9	9	8	6	2	−2
South Coast	−2	−1	2	4	7	9	10	10	9	6	1	−2
Southeast	−7	−3	−1	3	8	10	10	10	9	4	−3	−6
Interior	−4	−3	−3	−1	3	9	10	10	10	6	0	−2
Colorado:												
E of 105° Longitude	−14	−12	−9	−3	4	10	10	10	7	1	−8	−11
W of 105° Longitude	−24	−20	−12	−6	−1	4	8	6	1	−6	−14	−21
Connecticut	−14	−13	−8	−1	5	10	10	10	7	1	−4	−12
Delaware	−9	−8	−3	0	8	10	10	10	10	4	−1	−8
District Columbia	−8	−7	−3	3	9	10	10	10	10	5	0	−7
Florida:												
N of 29° Latitude	−1	1	4	9	10	10	10	10	10	9	3	−1
S of 29° Latitude	4	7	8	10	10	10	10	10	10	10	9	5
Georgia	−5	−2	1	6	10	10	10	10	10	6	0	−3
Hawaii	10	10	10	10	10	10	10	10	10	10	10	10
Idaho	−17	−16	−11	−3	−5	4	10	9	3	−2	−11	−15
Illinois:												
N of 40° Latitude	−18	−16	−9	−1	4	10	10	10	7	1	−7	−16
S of 40° Latitude	−15	−12	−7	1	7	10	10	10	9	3	−6	−13
Indiana	−16	−13	−7	−1	4	10	10	10	7	1	−6	−14
Iowa	−23	−19	−13	−3	4	10	10	10	6	0	−12	−20
Kansas	−17	−12	−9	−3	5	10	10	10	7	0	−8	−13
Kentucky	−12	−9	−4	1	8	10	10	10	9	3	−4	−11
Louisiana	−3	0	3	8	10	10	10	10	10	7	2	−1
Maine	−24	−22	−16	−4	1	7	10	8	3	−2	−8	−20
Maryland	−9	−8	−3	3	9	10	10	10	10	4	−2	−8
Massachusetts	−15	−14	−7	−1	4	10	10	10	6	0	−4	−13
[D]Michigan:												
Lower Michigan	−18	−17	−12	−3	1	7	10	9	5	0	−6	−14
Upper Michigan	−21	−20	−15	−6	−1	6	9	9	4	−1	−9	−18
Minnesota	−31	−28	−20	−7	0	6	10	8	1	−3	−16	−28
Mississippi	−3	−1	2	7	10	10	10	10	10	7	1	−3
Missouri	−14	−11	−6	1	8	10	10	10	10	3	−5	−12
Montana	−28	−24	−19	−6	1	5	9	8	1	−5	−17	−23
Nebraska	−19	−14	−11	−3	4	9	10	10	5	−2	−10	−16
Nevada:												
N of 38° Latitude	−18	−13	−8	−3	1	5	9	7	2	−3	−11	−14
S of 38° Latitude	−9	−5	−1	1	9	10	10	10	10	4	−3	−6
New Hampshire	−18	−17	−9	−2	3	9	10	9	3	−1	−6	−16
New Jersey	−10	−9	−4	2	7	10	10	10	10	4	−1	−8
New Mexico:												
N of 34° Latitude	−14	−11	−7	−2	1	7	10	10	7	1	−8	−12
S of 34° Latitude	−7	−5	−1	6	10	10	10	10	10	7	−2	−5
New York:												
N of 42° Latitude	−21	−20	−13	−3	2	9	10	10	4	−1	−6	−18
S of 42° Latitude	−13	−13	−7	1	6	10	10	10	8	2	−3	−12
North Carolina	−9	−7	−3	1	7	10	10	10	8	1	−5	−8
North Dakota	−29	−27	−11	−6	1	8	10	10	3	−2	−17	−24
Ohio	−14	−13	−8	−2	6	10	10	10	7	1	−5	−13
Oklahoma	−12	−6	−5	1	7	10	10	10	10	4	−4	−9
Oregon:												
E of 122° Longitude	−17	−12	−6	−3	0	4	6	6	2	−3	−8	−12
W of 122° Longitude	−5	−3	−1	2	5	8	10	10	7	2	−3	−3
Pennsylvania:												
N of 41° Latitude	−17	−19	−13	−4	1	6	9	8	2	−1	−6	−16
S of 41° Latitude	−13	−14	−9	−1	5	10	10	10	7	2	−4	−12
Rhode Island	−11	−11	−5	1	6	10	10	10	8	3	−2	−10
South Carolina	−3	−2	0	6	10	10	10	10	10	7	1	−3
South Dakota	−24	−21	−16	−4	3	10	10	10	4	−2	−12	−21
Tennessee	−9	−7	−3	2	9	10	10	10	10	2	−3	−8

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TABLE 5 *Continued*

						Temperature Conversion °F = (°C × 1.8) + 32°						
State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Texas:												
N of 31° Latitude	−11	−8	−4	2	8	10	10	10	10	5	−3	−7
S of 31° Latitude	−1	1	4	10	10	10	10	10	10	10	3	1
Utah	−15	−11	−7	−2	2	8	10	10	7	2	−11	−12
Vermont	−20	−21	−12	−2	2	9	10	10	5	0	−6	−17
Virginia	−8	−7	−3	3	9	10	10	10	10	4	−2	−7
Washington:												
E of 122° Longitude	−13	−6	−3	1	4	7	10	10	7	1	−5	−7
W of 122° Longitude	−6	−2	−2	1	4	7	9	9	8	2	−2	−2
West Virginia	−13	−12	−7	−2	4	9	10	10	5	−2	−7	−12
Wisconsin	−25	−21	−15	−3	3	8	10	10	5	−1	−11	−21
Wyoming	−23	−17	−14	−6	0	5	10	10	3	−2	−13	−16

A A maximum phase separation temperature of 10°C (50°F) is specified, even if the 6-h 10th percentile minimum temperature for the area and month can be higher.

B The designated areas of Alaska are divided as follows:

Southern Region—The Aleutians, Kodiak Island, the coastal strip East of Longitude 141°, and the Alaskan Peninsula South of Latitude 52°.

South Mainland—The portion of Alaska South of Latitude 62°, except the Southern Region.

North of Latitude 62°—The specification test temperature must be agreed between the vendor and purchaser having regard to equipment design, expected weather conditions, and other relevant factors.

C The designated areas of California are divided by county as follows:

North Coast—Alameda, Contra Costa, Del Norte, Humbolt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity.

Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (excepting that portion lying east of the Los Angles County Aqueduct), Kings, Madera, Mariposa, Merced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada.

South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct).

Southeast—Imperial, Riverside, San Bernadino, Los Angeles (that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct).

D The designated areas of Michigan are divided as follows:

Lower Michigan—That portion of the state lying East of Lake Michigan.

Upper Michigan—That portion of the state lying North of Wisconsin and of Lake Michigan.

ANNEX

(Mandatory Information)

A1. TEST METHOD FOR WATER TOLERANCE (PHASE SEPARATION) OF SPARK-IGNITION ENGINE FUEL

A1.1 Scope

A1.1.1 This test method determines the ability of gasoline-oxygenate blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be exposed in use.

A1.1.2 The values stated in SI units are standard.

A1.1.3 This test method is state-of-the-art; however, it may be revised and eventually balloted for publication as a separate standard.

A1.2 Summary of Test Method

A1.2.1 The sample of fuel is cooled at a controlled rate to its expected use temperature and is periodically observed for both haze and phase separation. The apparatus of Test Method D 2500 or a dry ice-isopropyl alcohol bath may be used. A maximum cooling rate of 2°C (4°F)/min is specified because phase separation in gasoline-oxygenate blends has a relatively long but unpredictable induction period.

A1.3 Significance and Use

A1.3.1 Some oxygenate-containing fuels, and gasoline-alcohol blends in particular have a very limited ability to retain water in solution or in stable suspension, and if the amount of water in the blend exceeds this limit, the fuel will separate into a lower oxygenate-rich aqueous phase and an upper oxygenate-lean hydrocarbon phase. The most important factor governing the ability of a specific fuel to retain water without such separation is its temperature. This method is intended to determine the maximum temperature at which the fuel will separate. The 10th percentile 6-h minimum temperature, or 10°C (50°F) whichever is lower, for the time of year and geographic area of the United States in which the fuel may be used, are tabulated in Table 3 of Specification D 4814. The temperatures represent the maximum temperatures above which the fuel must not separate into two distinct phases.

A1.3.2 Note that in this test, actual separation of the sample into two distinct phases is the criterion for failure. The following are indications of phase separation:

A1.3.2.1 The formation of droplets large enough to be detected by the unaided eye. They can be either clinging to the sides of the container or collect on the bottom.

A1.3.2.2 The formation of two layers separated by either a common boundary, or a layer of emulsion.

A1.3.3 Formation of haze without one of these indications of separation is not cause for rejection.

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A1.4 Apparatus

A1.4.1 *Test Container*—The container may be as specified in the apparatus section of Test Method D 2500, but any glass container of about 100 mL capacity may be used. This container may be marked at the level of 40 mL.

A1.4.2 *Thermometers,* meeting the requirements of Specification E 1. ASTM thermometer 6C (range −80 to +20°C, 1°C graduations, 76 mm immersion. Thermometer 6F is the Fahrenheit equivalent of 6C) spans the necessary range of temperatures. A thermometer must be provided for each container, mounted to pass through the stopper.

A1.4.3 *Viton Rubber Stopper*—to fit sample container, bored centrally for the test thermometer.

A1.4.4 *Cooling Bath*—May be of similar dimensions to those specified in 6.7 of Test Method D 2500 and provided with a jacket, disk, and gasket as specified in the apparatus section, filled with an equal-volume mixture of water and "permanent" antifreeze and provided with refrigeration coils capable of reducing its temperature to −40°C (−40°F). Alternatively, a dry ice-isopropyl alcohol bath may be used.

A1.5 Sampling and Handling

A1.5.1 Draw samples in accordance with the instructions in Practice D 4057, specifically 7.8.3, 7.9.1, and 10.3, except that water displacement, 10.3.1.8, shall not be used.

A1.5.2 Draw the samples in steel cans that have been solvent washed in accordance with 6.3.3.1 of Practice D 4306.

A1.5.3 Store the samples in a refrigerator (2 to 7°C, 35 to 45°F) whenever not actually transferring sample.

A1.5.4 Because gasoline-alcohol blends are hygroscopic as well as volatile, minimize contact with the atmosphere by keeping sample containers tightly closed except when transferring sample.

A1.6 Procedure

A1.6.1 Warm the sample to 15°C (59°F) and shake, to redissolve any water that may have settled out at the refrigerator temperature.

A1.6.2 Cool the test containers to 10 to 15°C (50 to 59°F). Carry out steps A1.6.3 through A1.6.5 as promptly as possible to minimize vaporization losses and absorption of water from the atmosphere.

A1.6.3 Rinse out the cooled test container with some of the sample to be tested. Drain.

A1.6.4 Pour about 40 mL of the sample into the test container. The precise amount is not critical, but it must be enough to submerge the thermometer bulb adequately, without being so much as to require an excessive amount of cooling time. If the sample has separated, as defined in A1.3.2, terminate the test.

A1.6.5 Seal the test container with the rubber stopper. Locate the thermometer bulb approximately at the center of the fuel sample.

A1.6.6 Cool the sample by intermittent immersion in or circulation of the coolant. The sample is not to be swirled or shaken while in the cooling bath. Starting at a cooling bath temperature not higher than 10°C (50°F), or 16°C (30°F) above the test temperature, cool the sample at a maximum rate of 2°C (4°F)/minute until phase separation occurs, or the test temperature is reached.

A1.6.7 At 2°C (4°F) intervals, remove the test container from the cooling bath and shake vigorously for 5 to 10 s. Wipe the exterior of the sample container with a towel moistened with isopropyl alcohol to remove any condensation, and observe the condition of the sample for no more than 5 s against a light colored, illuminated background.

A1.6.8 It is likely that the sample will get hazy prior to actual phase separation as defined in A1.3.2. Record the sample temperature at the first indication of haze (when cooling); and the temperature when the haze disappears (warming).

A1.6.9 Record the temperature of phase separation (A1.3.2). Then allow the sample to warm at ambient temperature. Shake the sample vigorously after a temperature rise of 2°C (4°F), and observe. Record a "warming" phase recombination temperature, and haze disappearance temperature. Average these "cooling" and "warming" temperatures to determine the actual phase separation and haze point temperatures. Repeat this process for improved accuracy.

A1.7 Report

A1.7.1 Report the following information:

A1.7.1.1 Report the averaged haze point and phase separation temperatures found in A1.6.9.

A1.8 Precision and Bias

A1.8.1 *Precision*—The precision of this test method has not been determined.

A1.8.2 *Bias*—There being no criteria for measuring bias in these test-product combinations, no statement of bias can be made.

APPENDIXES

(Nonmandatory Information)

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR AUTOMOTIVE SPARK-IGNITION ENGINE FUEL

X1.1 General

X1.1.1 Antiknock rating and volatility define the general characteristics of automotive spark-ignition engine fuel. Other characteristics relate to the following: limiting the concentration of undesirable components so that they will not adversely affect engine performance and ensuring the stability of fuel as well as its compatibility with materials used in engines and their fuel systems.

X1.1.2 Fuel for spark-ignition engines is a complex mixture composed of relatively volatile hydrocarbons that vary widely in their physical and chemical properties and may contain oxygenates. Fuel is exposed to a wide variety of mechanical, physical, and chemical environments. Thus, the properties of fuel must be balanced to give satisfactory

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engine performance over an extremely wide range of operating conditions. The prevailing standards for fuel represent compromises among the numerous quality and performance requirements. This ASTM specification is established on the basis of the broad experience and close cooperation of producers of fuel, manufacturers of automotive equipment, and users of both.

X1.2 Engine Knock

X1.2.1 The fuel-air mixture in the cylinder of a spark-ignition engine will, under certain conditions, autoignite in localized areas ahead of the flame front that is progressing from the spark. This is engine spark knock which can cause a ping that may be audible to the customer.

X1.2.2 The antiknock rating of a fuel is a measure of its resistance to knock. The antiknock requirement of an engine depends on engine design and operation, as well as atmospheric conditions. Fuel with an antiknock rating higher than that required for knock-free operation does not improve performance.

X1.2.3 A decrease in antiknock rating may cause vehicle performance loss. However, vehicles equipped with knock limiters can show a performance improvement as the antiknock quality of the fuel is increased in the range between customer audible knock and knock-free operation. The loss of power and the damage to an automotive engine due to knocking are generally not significant until the knock intensity becomes very severe. Heavy and prolonged knocking may cause power loss and damage to the engine.

X1.3 Laboratory Octane Number

X1.3.1 The two recognized laboratory engine test methods for determining the antiknock rating of fuels are the Research method (Test Methods D 2699 or D 2885) and the Motor method (Test Methods D 2700 or D 2885). The following paragraphs define the two methods and describe their significance as applied to various equipment and operating conditions.

X1.3.2 Research octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under mild operating conditions; namely, at a moderate inlet mixture temperature and a low engine speed. Research octane number tends to indicate fuel antiknock performance in engines at wide-open throttle and low-to-medium engine speeds.

X1.3.3 Motor octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under more severe operating conditions than those employed in the Research method; namely, at a higher inlet mixture temperature and at a higher engine speed. It indicates fuel antiknock performance in engines operating at wide-open throttle and high engine speeds. Also, Motor octane number tends to indicate fuel antiknock performance under part-throttle, road-load conditions.

X1.4 Road Octane Number

X1.4.1 The road octane of a fuel is the measure of its ability to resist knock in customers' vehicles, and is ultimately of more importance than laboratory octane numbers. Since road octanes are difficult to measure and interpret, the industry has agreed to use ASTM laboratory engine tests to estimate the road octane performance of spark-ignition engine fuel in vehicles.

X1.4.2 The antiknock index (AKI) is the arithmetic average of the Research octane number (RON) and Motor octane number (MON):

$$AKI = (RON + MON)/2 \qquad (X1.1)$$

This value is called by a variety of names, in addition to antiknock index, including:

Octane rating
Posted octane
(R + M)/2 octane

X1.4.3 The AKI is posted on retail gasoline dispensing pumps in the United States and is referred to in car owners' manuals. The AKI is also required for certification at each wholesale fuel transfer and is referred to in United States federal law as "Octane Rating." [9]

X1.4.4 The most extensive data base that relates the laboratory engine test methods for Research and Motor octane to actual field performance of fuel in vehicles is the annual Coordinating Research Council (CRC)[10] Octane Number Requirement Survey conducted for new light-duty vehicles. Analysis of these data shows that the antiknock performance of a fuel in some vehicles may correlate best with Research octane number, while in others, it may correlate best with Motor octane number. These correlations also differ from model year-to-model year or from vehicle population-to-vehicle population, reflecting changes in engine designs over the years.

X1.4.5 The antiknock index of a fuel approximates the CRC road octane ratings for many vehicles. However, the user must be guided also by experience as to which fuel is most appropriate for an individual vehicle. The antiknock index formula is reviewed periodically and may have to be adjusted in the future as engines and fuels continue to evolve. The present (RON + MON)/2 formula is an estimate and is not an absolute measure of fuel antiknock performance in general or in any specific vehicle.

X1.4.6 Car antiknock requirements vary, even within a single model, so the statistical distribution of the octane needs of any car population are usually shown in graphical form, as shown in Fig. X1.1. As antiknock index increases, larger and larger fractions of the car population in question will be free of knock, that is, be "satisfied" with the octane quality of fuels at or above that level of antiknock index. The data in Fig. X1.1 are for new model cars and trucks sold in the United States in the model year 1988 and are included as an example of the antiknock requirement distribution, not as a data reference.

X1.4.7 According to the winter 1988–1989 motor gasoline survey published by the National Institute for Petroleum and Energy Research, unleaded fuel antiknock indexes in current practice range from a low near 84 in the mountain areas to a high of near 94. Companies typically market two or three unleaded grades of fuel, one of which usually has a

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[9] Details of this regulation can be found in Code of Federal Regulations Title 16, Chapter 1, Subchapter C, part 306 (16 CFR 306), U.S. Government Printing Office, Superintendent of Documents, Washington DC 20402.

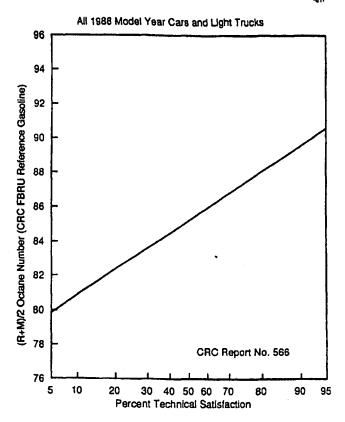[10] Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA 30346.

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All 1988 Model Year Cars and Light Trucks

FIG. X1.1 An Example of the Statistical Distribution of Vehicle Antiknock Requirements

TABLE X1.1 Automotive Spark-Ignition Engine Fuel Antiknock Indexes in Current Practice

Unleaded Fuel[A] (for vehicles that can or must use unleaded fuel)	
Antiknock Index[B,C,D,E] (RON + MON)/2	Application
87	Designed to meet antiknock requirements of most 1971 and later model vehicles
89	Satisfies vehicles with somewhat higher antiknock requirements
91 and above	Satisfies vehicles with high antiknock requirements

Leaded Fuel (for vehicles that can or must use leaded fuel)	
Antiknock Index[B,C,D,E] (RON + MON)/2	Application
88	For most vehicles that were designed to operate on leaded fuel

[A] Unleaded fuel having an antiknock index of at least 87 should also have a minimum Motor octane number of 82 in order to adequately protect those vehicles that are sensitive to Motor octane quality.

[B] Reductions in vehicle antiknock requirements for altitude are shown in Fig. X1.2.

[C] Reductions in vehicle antiknock requirements for seasonal variations are shown in Fig. X1.3.

[D] Not all antiknock index levels listed in this table are available at all locations.

[E] The Federal Trade Commission requires octane posting and certification in accordance with 16 CFR Part 306.

minimum antiknock index of 87, for which most post-1971 vehicles are designed. Most companies also market a higher octane fuel with an antiknock index of 91 or above. This fuel is intended to satisfy those vehicles with a higher octane requirement. Some companies offer three grades of unleaded fuel. The third grade usually has an antiknock index of 89. Leaded fuel is still available in some markets and usually has an antiknock index of 88 or 89.

X1.4.8 Marketers set the grades and octane based on their perception of the technical and competitive needs in the market.

X1.4.9 Antiknock indexes of fuel sold in current practice in the United States are shown in Table X1.1 for both unleaded and leaded fuels.

X1.5 Precision and Bias of Antiknock Index

X1.5.1 The following statements apply to the precision and bias of antiknock index of fuel, which is a composite quantity not addressed in any other standard.

X1.5.2 The precision of the antiknock index, (RON + MON)/2, is a function of the individual precisions of Research (Test Method D 2699) and Motor (Test Method D 2700) octane numbers. The repeatability and reproducibility variances for these test methods are summed and divided by four to obtain the variance of the antiknock index.

X1.5.2.1 *Repeatability*—The difference between two sets of antiknock index determinations, where two test results by

each octane number method were obtained by one operator, with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

X1.5.2.2 *Reproducibility*—The difference between two independent sets of antiknock index determinations, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

Antiknock Index	Repeatability Limits, Antiknock Index Units	Reproducibility Limits, Antiknock Index Units
83	0.2	0.7
85	0.2	0.7
87	0.2	0.7
89	0.2	0.6
91	0.2	0.6
93	0.2	0.6
95	—	0.6
97	—	0.7

NOTE X1.1—These precision limits were calculated from Research and Motor octane number results obtained by member laboratories of the ASTM National Exchange Group (NEG) participating in a cooperative testing program. The data obtained during the period 1980 through 1982 have been analyzed in accordance with RR:D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants," Spring, 1973.

X1.5.2.3 *Bias*—Since knock ratings are determined by the conditions of the empirical test methods involved, bias cannot be determined.

X1.6 Effects of Altitude and Weather on Vehicle Antiknock Requirement

X1.6.1 A vehicle's antiknock requirement can vary with changes in altitude, ambient temperature, and humidity, depending on the control system of the vehicle. New vehicles have sensors to measure, and engine management computers

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which take into account, such conditions as air charge temperature and barometric pressure. These vehicles are designed to have the same antiknock requirement at all altitudes and a reduced sensitivity to changes in ambient temperature. This more sophisticated control technology began to be used extensively in 1984. This technology, while constantly evolving and improving, is used on almost all new vehicles. This means that many vehicles in today's fleet require fuel having the same antiknock index regardless of changes in altitude or ambient temperatures. Older vehicles which do not have sophisticated control systems will likely experience changes in antiknock requirement due to changes in altitude and weather conditions. However, the changes in antiknock requirement indicated in the following sections apply to a continually smaller part of the vehicle fleet.

X1.6.2 The antiknock requirement of an older vehicle decreases as altitude increases, primarily due to reduction in mixture density caused by reduced atmospheric pressure. The change in antiknock requirement for altitude for older vehicles is given in Fig. X1.2. Boundaries of the areas defined and the corresponding antiknock index reductions were established to protect vehicles driven from a higher altitude to a lower altitude (and, hence higher antiknock requirement) area while using a fuel obtained in the high altitude area.

X1.6.3 Tests by CRC and other organizations have shown that the decrease in antiknock requirements with altitude is larger for most models between 1971 and 1984, designed to

use a fuel with an antiknock index of 87, than for pre-1971 vehicles. Generally the pre-1971 vehicles have high compression ratios and were designed for fuels with an antiknock index of 88 or higher. Fuels with antiknock indexes below 89 are adjusted by a larger factor than those with an antiknock index of 89 or greater.

X1.6.4 The antiknock requirements of older vehicles rise with increasing ambient temperature on the average by 0.097 MON per degree Celsius (0.054 MON per degree Fahrenheit).

X1.6.5 The antiknock requirements of both older and new vehicles decrease with increasing specific humidity by 0.245 MON per gram of water per kilogram of dry air (0.035 MON per grain of water per pound of dry air).

X1.6.6 Because temperature and humidity of geographical areas are predictable throughout the year from past weather records, antiknock index levels can be adjusted to match seasonal changes in vehicle antiknock requirements. Fig. X1.3 defines the boundaries of areas and the typical reduction in vehicle antiknock requirements for weather for older vehicles. This figure may not apply to newer vehicles.

X1.7 Leaded Versus Unleaded Fuel Needs

X1.7.1 In addition to selecting the appropriate antiknock index to meet vehicle antiknock needs, a choice must be made between leaded and unleaded fuel. Vehicles that must use unleaded fuel are required by Environmental Protection Agency regulation to have permanent labels on the instrument panel and adjacent to the fuel tank filler inlet reading "Unleaded Fuel Only." Most 1975 and later model passenger cars and light trucks are in this category. Most 1971–1974 vehicles can use leaded or unleaded fuel. Pre-1971 vehicles were designed for leaded fuel; however, unleaded fuel of suitable antiknock index may generally be used in these vehicles, except that leaded fuel should be used periodically (after a few tankfuls of unleaded fuel have been used). Leaded fuel may be required in some vehicles, particularly trucks, in heavy-duty service and some farm equipment. Instructions on fuel selection are normally provided in publications of vehicles manufacturers (for example, owner's manuals, service bulletins, etc.). Antiknock agents other than lead alkyls may be used to increase the antiknock index of fuels, and their concentrations may also be limited due to either performance or legal requirements.

X1.8 Volatility

X1.8.1 In most spark-ignition internal combustion engines, the fuel is metered in liquid form through the carburetor or fuel injector, and is mixed with air and partially vaporized before entering the cylinders of the engine. Consequently, volatility is an extremely important characteristic of motor fuel.

X1.8.2 At high operating temperatures, fuels can boil in fuel pumps, lines, or carburetors. If too much vapor is formed, the fuel flow to the engine can be decreased, resulting in loss of power, rough engine operation, or engine stoppage. These conditions are known as "vapor lock." Conversely, fuels that do not vaporize sufficiently can cause hard starting of cold engines and poor warm-up performance. These conditions can be minimized by proper selection of volatility requirements, but cannot always be

FIG. X1.2 Reduction in Vehicle Antiknock Requirements for Altitude [A,B]

Area	Less than 89 AKI	89 AKI or Greater
I	0.7	0.5
II	1.5	1.5
III	2.2	1.5
IV	3.0	2.0
V	4.5	3.0

[A] Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

[B] While the reductions in this table apply to most pre-1984 vehicles, the control technology on almost all new vehicles will cause them to have no reduction in antiknock requirement at higher altitudes.

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FIG. X1.3 Reduction in Vehicle Antiknock Requirements for Weather[A]

	J	F	M	A	M	J	J	A	S	O	N	D
Northeast	1.0	0.5	0.5	0	0	0	0	0	0	0.5	0.5	1.0
Southeast	0.5	0	0	0	0	0.5	0.5	0.5	0.5	0	0	0.5
Midwest	1.0	0.5	0.5	0	0	0	0	0	0	0	0.5	1.0
Northwest	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Southwest	1.0	0.5	0	0	0	0	0	0	0	0	0.5	1.0
California [B]												
No Coast	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0.5	0.5
So Coast	0	0	0.5	0.5	1.0	1.0	1.0	0.5	0.5	0	0	0
Alaska	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Hawaii	0	0	0	0	0	0	0	0	0	0	0	0

[A] Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

[B] Details of California coastal areas are shown in Footnote C of Table 4.

avoided. For example, during spring and fall a fuel of volatility suitable for satisfactory starting at low ambient temperatures can cause problems in some engines under higher ambient temperature operating conditions.

X1.8.3 Six vapor pressure/distillation classes and five vapor lock protection (vapor-liquid ratio) classes of fuel are provided to satisfy vehicle performance requirements under different climatic conditions and to comply with U.S. EPA vapor pressure limits for the control period of May 1 through September 15. Class A and Class AA specify the EPA maximum vapor pressure limits of 9.0 psi and 7.8 psi, respectively. Volatility of fuel is specified by an alphanumeric designation. The letter specifies the vapor pressure/distillation class and the number specifies the vapor lock protection class. The vapor pressure/distillation classes are needed to comply with the EPA vapor pressure regulations and are not based on vehicle performance during the EPA control period. The separate vapor lock protection classes are provided because under most ambient conditions the EPA regulations specify a lower vapor pressure than would be required to prevent hot fuel handling problems. If the corresponding and unnecessarily more restrictive vapor-liquid ratios were specified when the EPA regulations are in effect, it could result in reduced fuel production, manufacturing hardships, and increased fuel costs. The schedule for seasonal and geographical distribution indicates the appropriate alphanumeric volatility requirement or requirements for each month in all areas of the United States, based on altitude and expected air temperatures, and on EPA vapor pressure regulations. Volatility limits are established in terms of vapor-liquid ratio, vapor pressure, and distillation properties.

X1.8.4 For sea-level areas outside of the United States

where vapor pressure requirements are not as restrictive as those specified by EPA, the following ambient temperatures are for guidance in selecting the appropriate alphanumeric designation:

Alphanumeric Volatility Designation	10th Percentile 6-h Minimum Daily Temperature, °C (°F)	90th Percentile Maximum Daily Temperature, °C (°F)
A-1	>16 (60)	≥43 (110)
B-2	>10 (50)	<43 (110)
C-3	>4 (40)	<36 (97)
D-4	>−7 (20)	<29 (85)
E-5	≤−7 (20)	<21 (69)

The 6-h minimum temperature is the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. The 6-h minimum temperature provides information on the cold-soak temperature experienced by a vehicle. The 10th percentile of this temperature statistic indicates a 10 % expectation that the 6-h minimum temperature will be below this value during a month. The 90th percentile maximum temperature is the highest temperature expected during 90 % of the days, and provides information relative to peak vehicle operating temperatures during warm and hot weather. For areas above sea level, the 10th percentile 6-h minimum temperature should be increased by 3.6°C/1000 m (2°F/1000 ft) of altitude, and the 90th percentile maximum should be increased by 4.4°C/1000 m (2.4°F/1000 ft) of altitude before comparing them to the sea level temperature. These corrections compensate for changes in fuel volatility caused by changes in barometric pressure due to altitude.

X1.9 Vapor Pressure

X1.9.1 The vapor pressure of fuel must be sufficiently high to ensure ease of engine starting, but it must not be so high as to contribute to vapor lock or excessive evaporative emissions and running losses.

X1.9.2 Test Methods D 4953, D 5190, D 5191, or D 5482 provide procedures for determining the vapor pressures of gasoline or gasoline-oxygenate blends.

X1.10 Vapor-Liquid Ratio

X1.10.1 Vapor-liquid ratio (V/L) is the ratio of the volume of vapor formed at atmospheric pressure to the volume of fuel tested in Test Method D 2533. The V/L increases with temperature for a given fuel. Because some oxygenates are miscible with the glycerin confining fluid, Test Method D 2533 has been modified so mercury can also be used as a confining fluid. Either procedure may be used for determining V/L of gasoline. The mercury confining fluid shall be used for gasoline-oxygenate blends. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. Test Method D 5188 is applicable to both gasoline and gasoline-oxygenate blends.

X1.10.2 The temperature of the fuel system and the V/L that can be tolerated without vapor lock vary from vehicle to vehicle and with operating conditions. The tendency of a fuel to cause vapor lock, as evidenced by loss of power during full-throttle accelerations, is indicated by the gasoline temperature at a V/L of approximately 20. A similar relationship for gasoline-oxygenate blends has also been determined. The temperature at which the maximum V/L is specified for

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each gasoline volatility class is based on the ambient temperatures and the altitude associated with the use of the class.

X1.11 Vapor-Liquid Ratio (Estimated)

X1.11.1 Three techniques for estimating temperature-V/L values using vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) results are given in Appendix X2; they apply to gasoline only.

X1.12 Distillation

X1.12.1 Test Method D 86 for distillation provides another measure of the volatility of fuels. Table 1 designates the limits for end-point temperature and the temperatures at which 10 %, 50 %, and 90 % by volume of the fuel is evaporated. These distillation characteristics, along with vapor pressure and V/L characteristics, affect the following vehicle performance characteristics: starting, driveability, vapor lock, dilution of the engine oil, fuel economy, and carburetor icing.

X1.12.2 The 10 % evaporated temperature of fuel should be low enough to ensure starting under normal temperatures.

X1.12.3 Fuels having the same 10 % and 90 % evaporated temperatures can vary considerably in driveability performance because of differences in the boiling temperatures of the intermediate components, or fractions. Driveability and idling quality are affected by the 50 % evaporated temperature. The 90 % evaporated and end-point temperatures should be low enough to minimize dilution of the engine oil.

X1.13 Corrosion

X1.13.1 Fuels must pass the copper strip corrosion test to minimize corrosion in fuel systems due to sulfur compounds in the fuel. Some fuels corrode fuel system metals other than copper, but there are no ASTM test methods to evaluate corrosion of these metals. Depending on the type and concentration of oxygenate, gasoline-oxygenate blends can corrode metals such as zinc, magnesium, aluminum, steel, and terne. However, at this time there is no test method with a known correlation to field performance. Consequently, additional corrosion tests are needed.

X1.14 Solvent-Washed Gum Content

X1.14.1 The test for solvent-washed gum content measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, non-volatile material such as additives, carrier oils used with additives, and heavier hydrocarbons such as diesel fuels, etc. Solvent-washed gum consists of fuel-insoluble gum and fuel-soluble gum. The fuel-insoluble portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

X1.14.2 Solvent-washed gum can contribute to deposits on the surfaces of carburetors, fuel injectors, and intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum on malfunctions of modern engines is not well established and the current specification limit is historic rather than the result of recent correlative studies. It depends on where the deposits form, the presence of other deposit precursors such as airborne debris, blowby and exhaust gas recirculation gases, and oxidized engine oil, and the amount of deposits.

X1.14.3 The difference between the unwashed and solvent-washed gum content values can be used to assess the presence and amount of nonvolatile material in the fuel. Additional analytical testing is required to determine if the material is additive, carrier oil, diesel fuel, etc.

X1.15 Sulfur

X1.15.1 The limit on sulfur content is included to protect against engine wear, deterioration of engine oil, and corrosion of exhaust system parts.

X1.16 Oxidation Stability

X1.16.1 The induction period as measured in the oxidation stability test is used as an indication of the resistance of fuel to gum formation in storage. Experience indicates that fuels with an induction period equal to or greater than that in Table 3 generally have acceptable short-term storage stability. However, correlation of the induction period with the formation of gum in storage can vary markedly under different storage conditions and with different fuels.

X1.17 Water Tolerance

X1.17.1 Water tolerance is the ability of a fuel to dissolve water without phase separation. It is not of concern for gasoline because of the very low solubility of water in hydrocarbons. Water tolerance is of some concern with gasoline-ether blends because of the limited solubility of ethers in water, but it is of great concern for gasoline-alcohol blends because of the very high solubility of alcohols in water. If the amount of water exceeds the water tolerance limit of the blend, the fuel will separate into a lower alcohol-rich aqueous phase and an upper alcohol-lean hydrocarbon phase. The resultant aqueous phase is not suitable as an automotive fuel and may be corrosive to many metals. Similarly, the hydrocarbon portion may also not be suitable as a fuel since removal of the alcohol component will change the volatility and antiknock characteristics.

X1.17.2 The most important factor, besides the quantity of water contacted, which governs the water tolerance of a fuel is its temperature. As the temperature of the blend decreases, water tolerance decreases. The test method found in Annex A1 is intended to determine the ability of gasoline-oxygenate blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be exposed in use. Some other factors that affect water tolerance are concentration and type of oxygenate and aromatics content of the fuel.

X1.17.3 With some gasoline-oxygenate blends, formation of a haze may occur when filling a storage tank that contains water bottoms, while commingling of gasoline-oxygenate blends with gasoline, or when a sufficient decrease in temperature occurs. However, the haze may not be stable and the fuel will clear usually in a short period of time.

X1.17.4 A more critical water tolerance concern is the potential increase in storage tank water bottoms. This can occur when some gasoline-oxygenate blends and gasoline-alcohol blends in particular are added to a tank that contains sufficient water to extract some or all of the oxygenate component from the fuel.

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X2. ESTIMATING TEMPERATURE-V/L VALUES FOR GASOLINE

X2.1 Scope

X2.1.1 Three techniques are presented here for estimating temperature-V/L data from vapor pressure and distillation test results[11] on gasolines only. They are provided for use as a guideline when V/L data measured by Test Method D 2533 are not available. One method is designed for computer processing, one is a simpler linear technique, while the other is a nomogram form of this linear equation.

X2.1.2 These techniques are not optional procedures for measuring V/L. They are supplementary tools for estimating temperature-V/L relationships with reasonable accuracy when used with due regard for their limitations.

X2.1.3 Test Method D 2533 is the referee V/L procedure and shall be used when calculated values are questionable.

X2.1.4 These techniques are not intended for, nor are they necessarily applicable to, fuels of extreme distillation or chemical characteristics such as would be outside the range of normal commercial motor gasolines. Thus, they are not applicable in all instances to gasoline blending stocks or specially blended fuels.

X2.2 Computer Method

X2.2.1 *Summary*—The values of four intermediate functions, A, B, C, and D, are derived from the gasoline vapor pressure and distillation temperatures at 10, 20, and 50 % evaporated. Values for A, B, C, and D can be obtained either from equations or from a set of charts. Sections X2.2.2.1 through X2.2.2.3 provide A, B, C, and D values using SI units; X2.2.2.6 through X2.2.2.8 provide A, B, C, and D values using inch-pound units. Estimated temperatures at a V/L of 4, 10, 20, 30, and 45 are then calculated from A, B, C, and D. Estimated temperatures at an intermediate V/L can be obtained by interpolation.

X2.2.2 *Procedure:*

X2.2.2.1 Establish input data from vapor pressure (Test Methods D 4953, D 5190, D5191, or D 5482) and distillation (Test Method D 86) test results as follows:

E = distillation temperature, °C at 10 % evaporated,
F = distillation temperature, °C at 20 % evaporated,
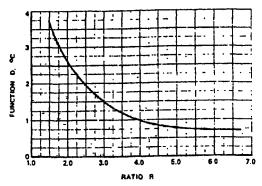G = distillation temperature, °C at 50 % evaporated,
$H = G - E$, °C, $\qquad$ (X2.1)
P = vapor pressure, kPa,
$Q = F - E$, °C, and $\qquad$ (X2.2)
$R = H/Q$, except that if H/Q is greater than 6.7,
$\quad$ make $R = 6.7$. $\qquad$ (X2.3)

X2.2.2.2 If A, B, C, and D, are to be calculated use the following equations:

$$A = 102.859 - 1.36599P + 0.009617\,P^2 - 0.000028281P^3 \quad \text{(X2.4)}$$
$$+ 207.0097/P$$

$$B = -5.36868 + 0.910540Q - 0.040187\,Q^2 \quad \text{(X2.5)}$$
$$+ 0.00057774Q^3 + 0.254183/Q$$

$$S = -0.00525449 - 0.3671362/(P - 9.65) - 0.812419$$
$$/(P - 9.65)^2 + 0.0009677R - 0.0000195828R^2 - \quad \text{(X2.6)}$$
$$+ 3.3502318R/P^2 + 1241.1531R/P^4 - 0.06630129R^2$$
$$/P + 0.00627839R^3/P + 0.0969193R^2/P^2$$

$$C = 0.34205P + 0.55556/S \quad \text{(X2.7)}$$

$$D = 0.62478 - 0.68964R + 0.132708R^2 \quad \text{(X2.8)}$$
$$+ - 0.0070417R^3 + 5.8485/R$$

X2.2.2.3 If A, B, C, and D, are to be obtained from charts, read them from Figs. X2.1, X2.2, X2.3, and X2.4, respectively.

X2.2.2.4 Calculate the estimated temperature (°C or °F) at V/L ratios 4, 10, 20, 30, and 45 from the following equations:
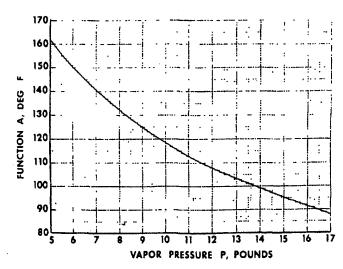
$$T4 = A + B \quad \text{(X2.9)}$$
$$T45 = F + 0.125H + C \quad \text{(X2.10)}$$

FIG. X2.1 Function A versus Vapor Pressure P

FIG. X2.2 Function B versus Distillation Temperature Difference Q

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FIG. X2.3 Function C versus Ratio R and Vapor Pressure P

FIG. X2.4 Function D versus Ratio R

$$T10 = T4 + 0.146341\,(T45 - T4) + D \qquad (X2.11)$$
$$T20 = T4 + 0.390244\,(T45 - T4) + 1.46519D \qquad (X2.12)$$
$$T30 = T4 + 0.634146\,(T45 - T4) + D \qquad (X2.13)$$

where:
$T4$, $T10$, $T20$, $T30$, and $T45$ are estimated temperatures at V/L ratios, 4, 10, 20, 30, and 45.

X2.2.2.5 If the temperature at an intermediate V/L ratio is to be estimated, either plot the values calculated in X2.2.2.4 and read the desired value from a smooth curve through the points, or use the Lagrange interpolation formula as follows:

$$TX = T4\left(\frac{X-10}{4-10} \times \frac{X-30}{4-30} \times \frac{X-45}{4-45}\right)$$
$$+ T10\left(\frac{X-4}{10-4} \times \frac{X-30}{10-30} \times \frac{X-45}{10-45}\right)$$
$$+ T30\left(\frac{X-4}{30-4} \times \frac{X-10}{30-10} \times \frac{X-45}{30-45}\right) \qquad (X2.14)$$
$$+ T45\left(\frac{X-4}{45-4} \times \frac{X-10}{45-10} \times \frac{X-30}{45-30}\right)$$

where:
X = the desired V/L ratio between 4 and 45, and
TX = the estimated temperature at V/L ratio X.

X2.2.2.6 If inch-pound units are used, establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:
E = distillation temperature, °F, at 10 % evaporated,
F = distillation temperature, °F, at 20 % evaporated,
G = distillation temperature, °F, at 50 % evaporated,

$$H = G - E, \text{ °F} \qquad (X2.15)$$
P = vapor pressure, psi,
$$Q = F - E, \text{ °F, and} \qquad (X2.16)$$
R = H/Q, except that if H/Q is greater than 6.7,
make $R = 6.7$. $\qquad (X2.17)$

X2.2.2.7 If A, B, C, and D are to be calculated in inch-pound units, use the following equations:

$$A = 217.147 - 16.9527P + 0.822909P^2 - 0.0166849P^3 \atop + 54.0436/P \qquad (X2.18)$$

$$B = -9.66363 + 0.910540Q - 0.0223260Q^2 \atop + 0.000178314Q^3 + 0.823553/Q \qquad (X2.19)$$

$$S = -0.00525449 - 0.0532486/(P - 1.4)$$
$$- 0.0170900/(P - 1.4)^2 + 0.0009677R -$$
$$0.0000195828R^2 - 0.0704753R/P^2 + 0.549224R/P^4 \quad (X2.20)$$
$$- 0.00961619R^2/P + 0.000910603R^3/P$$
$$+ 0.00203879R^2/P^2$$

$$C = 4.245P + 1.0/S \qquad (X2.21)$$

$$D = 1.12460 - 1.24135R + 0.238875R^2 \atop - 0.0126750R^3 + 10.5273/R \qquad (X2.22)$$

X2.2.2.8 If A, B, C, and D are to be obtained from charts in inch-pound units, read them from Figs. X2.5, X2.6, X2.7, and X2.8, respectively.

X2.2.2.9 Calculate the estimated temperatures, °F, at V/L

FIG. X2.5 Function A versus Vapor Pressure P

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FIG. X2.6 Function B versus Distillation Temperature
Difference Q

FIG. X2.8 Function D versus Ratio R

ratios 4, 10, 20, 30, and 45 using the equations in X2.2.2.4
and X2.2.2.5.

X2.3 Linear Equation Method

X2.3.1 *Summary*—As given, these two equations provide
only the temperatures (°C or °F) at which a V/L value of 20
exists. They make use of two points from the distillation
curve, T_{10} and T_{50} (°C or °F), and the vapor pressure (kPa or
psi) of the gasoline with constant weighting factors being
applied to each. Experience has shown that data obtained
with these simple linear equations generally are in close
agreement with those obtained by the computerized version
given above. The limitations pointed out in X2.1.1 through
X2.1.4 must be kept in mind when use is made of this
procedure.

X2.3.2 *Procedure*—Obtain 10 % evaporated and 50 %

FIG. X2.7 Function C versus Ratio R and Vapor Pressure P

evaporated points from the distillation curve (Test Method
D 86) along with the vapor pressure value (Test Methods
D 4953, D 5190, D 5191, or D 5482); apply these directly in
the equation.

$$T_{V/L-20} = 52.47 - 0.33 \text{ (VP)} + 0.20 \ T_{10} + 0.17 \ T_{50} \qquad \text{(X2.23)}$$

where:
$T_{V/L-20}$ = temperature, °C, at V/L of 20:1,
VP = vapor pressure, kPa,
T_{10} = distillation temperature, °C, at 10 % evaporated,
and
T_{50} = distillation temperature, °C, at 50 % evaporated.

or in the inch-pound customary unit equation:

$$T_{V/L-20} = 114.6 - 4.1 \text{ (VP)} + 0.20 \ T_{10} + 0.17 \ T_{50} \qquad \text{(X2.24)}$$

where:
$T_{V/L-20}$ = temperature, °F, at V/L of 20:1,
VP = vapor pressure, psi,
T_{10} = distillation temperature, °F, at 10 % evaporated,
and
T_{50} = distillation temperature, °F, at 50 % evaporated.

X2.4 Nomogram Method

X2.4.1 *Summary*—Two nomograms have been devel-
oped and are included herein (Figs. X2.9 and X2.10) to
provide the same function as the linear equations procedure
outlined above. Figure X2.9 is in SI units and Fig. X2.10 is
in inch-pound units. The nomograms are based on the two
equations and the same limitations apply to their use in
estimating V/L (20) temperatures.

X2.4.2 *Procedure*—Obtain 10 % evaporated and 50 %
evaporated points from the distillation curve (Test Method
D 86) along with the vapor pressure value (Test Methods
D 4953, D 5190, D 5191, or D 5482). Select the SI unit (Fig.
X2.9) or inch-pound unit (Fig. X2.10) nomogram based on
the units of T_{10}, T_{50}, and VP. Using a straightedge, locate the
intercept on the line between the "T_{10} and T_{50}" scales after
selecting the applicable T_{10} and T_{50} values. From this
intercept and the proper point on the "VP" scale, a second
intercept can be obtained on the "$T_{V/L-20}$" scale to provide
the desired value directly.

X2.5 Precision

X2.5.1 The precision of agreement between temperature-
V/L data estimated by any one of these three techniques and
data obtained by Test Method D 2533 has not been estab-
lished.

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NOMOGRAM SOLVES EQUATION

$T_{V/L=20}$ = 52.47 − 0.33 VP + 0.20 T_{10} + 0.17 T_{50}

where:

$T_{V/L=20}$ = TEMPERATURE (°C) FOR VAPOR/LIQUID RATIO OF 20:1
T_{10} = 10 % EVAPORATION POINT (°C)
T_{50} = 50 % EVAPORATION POINT (°C)
VP = VAPOR PRESSURE (kPa)

FIG. X2.9   Relationship Between Gasoline Volatility and Temperature for *V/L* Ratio at Sea Level—SI Units

NOMOGRAM SOLVES EQUATION

$T_{V/L=20}$ = 114.6 − 4.1 VP + 0.20 T_{10} + 0.17 T_{50}

where:

$T_{V/L=20}$ = TEMPERATURE (°F) FOR VAPOR/LIQUID RATIO OF 20:1
T_{10} = 10 % EVAPORATION POINT (°F)
T_{50} = 50 % EVAPORATION POINT (°F)
VP = VAPOR PRESSURE (psi)

FIG. X2.10   Relationship Between Gasoline Volatility and Temperature for *V/L* Ratio of 20 at Sea Level—Inch-Pound Units

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X3. SUMMARY OF EPA REGULATIONS APPLICABLE TO SPARK-IGNITION ENGINE FUEL

X3.1 EPA Applicable Vapor Pressure Standards

X3.1.1 Under authority of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) issued, effective May 1992, vapor pressure control standards for leaded and unleaded gasoline and leaded and unleaded gasoline-oxygenate blends. Some states, notably California, have more restrictive vapor pressure limits.

X3.1.2 Details of the EPA regulations and test methods are available in Part 80 of Title 40 of the Code of Federal Regulations (40 CFR Part 80). For specific state vapor pressure regulations, the state of interest should be contacted.

X3.1.3 The EPA maximum vapor pressure limits of 7.8 psi and 9.0 psi are shown in Table 1 as Classes AA and A, respectively. The EPA requirements for each distribution area are shown in Table 4 for the period May 1 through September 15. For the month of May, the EPA limits only apply to finished gasoline and gasoline-oxygenate blend tankage at refineries, importers, pipelines, and terminals. For the period June 1 through September 15, the EPA limits apply to all locations of the distribution system. Footnotes D through F of Table 4 indicate the ozone nonattainment areas which are limited to 7.8 psi maximum and the appropriate vapor lock protection class. California has controls that vary for the different air basins from as early as March 1 at refineries through as late as October 31. There are no EPA vapor pressure limits for the states of Alaska or Hawaii.

X3.1.4 EPA regulations allow 1.0 psi higher values for gasoline-ethanol blends than the EPA limits shown in Tables 1 and 4 for the period May 1 through September 15. To qualify, the gasoline-ethanol blends must contain 9 to 10 volume % ethanol. Higher vapor pressure limits for gasoline-ethanol blends under state regulations vary for other time periods, and specific states of interest should be contacted to determine if higher limits apply.

X3.2 EPA Lead and Phosphorus Regulations

X3.2.1 *Unleaded Fuel*—The intentional addition of lead or phosphorus compounds to unleaded fuel is not permitted by EPA. EPA regulations limit their maximum concentrations to 0.05 g lead per U.S. gallon (0.013 g/L) and 0.005 g of phosphorus per U.S. gallon (0.0013 g/L) (see Test Method D 3231), respectively.

X3.2.2 *Leaded Fuel*—EPA regulations limit the lead concentration in leaded fuel to no more than 0.10 g per U.S. gallon (0.026 g/L) averaged per calendar quarter for each refinery. There is no EPA lead limit for any individual gallon of leaded fuel.

X3.3 EPA Oxygenate Regulations Applicable to Unleaded Gasoline-Oxygenate Blends

X3.3.1 *Substantially Similar Rule:*

X3.3.1.1 Section 211(f) (1) of the Clean Air Act prohibits introducing into commerce or increasing the concentration in use of, any fuel or fuel additive, which is not substantially similar to any fuel or fuel additive utilized for emissions certification of any model year 1975, or subsequent model year vehicle or engine, unless a waiver is obtained from the EPA.

X3.3.1.2 Gasoline-oxygenate blends are considered "sub-

stantially similar" if the following criteria are met.

(1) The fuel must contain carbon, hydrogen, and oxygen, nitrogen, or sulfur, or combination thereof, exclusively, in the form of some combination of the following:

(a) Hydrocarbons;

(b) Aliphatic ethers;

(c) Aliphatic alcohols other than methanol;

(d) (i) Up to 0.3 volume % methanol;

(ii) Up to 2.75 volume % methanol with an equal volume of butanol, or higher molecular weight alcohol;

(2) The fuel must contain no more than 2.0 mass % oxygen except fuels containing aliphatic ethers and/or alcohols (excluding methanol) must contain no more than 2.7 mass % oxygen.

(3) The fuel must possess, at the time of manufacture, all of the physical and chemical characteristics of an unleaded gasoline as specified by Specification D 4814 – 88 for at least one of the Seasonal and Geographical Volatility Classes specified in the standard.

NOTE X3.1—Opinion varies as to whether the EPA "substantially similar" rule requires unleaded gasolines that do not contain oxygenates to meet ASTM specifications.

X3.3.2 *Waivers:*

X3.3.2.1 EPA has issued waivers for blends of gasoline and ethanol (gasohol), gasoline and ethanol with cosolvents, and gasoline and methanol with cosolvents that are less limiting than the "substantially similar" rule. For the latest listing of waivers, EPA should be contacted.

X3.3.2.2 Gasoline-ethanol blends are not required by EPA to meet Specification D 4814 volatility limits (see X3.1.4 for vapor pressure limits). EPA has specified in all other waivers that the volatility of the finished gasoline-oxygenate blend must comply with Specification D 439 or D 4814 climatic and geographical limits.

X3.4 EPA Reformulated Gasoline (RFG)

X3.4.1 Reformulated gasoline (RFG) is a spark-ignition engine fuel formulated to reduce motor vehicle emissions of toxic and tropospheric ozone-forming compounds. The Clean Air Act Amendments of 1990 require that RFG be sold in nine metropolitan areas with the worst summertime ozone levels. Other areas that do not meet ambient ozone standards may petition EPA to require RFG. The various RFG regulations have been established by the EPA. EPA has also placed limits on conventional gasoline sold in the rest of the U.S. to prevent RFG producers from using conventional gasoline as an outlet for undesirable fuel components (anti-dumping requirements). The EPA requirements became effective at the retail level on January 1, 1995.

X3.4.2 The characteristics of reformulated spark-ignition engine fuel, beyond those described by this specification, are described in the research report on reformulated spark-ignition engine fuel.[2] The research report also includes information on California Air Resources Board Phase 2 gasoline requirements, which are more restrictive than the EPA RFG requirements and take effect at the retail level on June 1, 1996.

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X4. METHOD FOR CALCULATING MASS PERCENT OXYGEN OF GASOLINE-OXYGENATE BLENDS

X4.1 Scope

X4.1.1 Test Method D 4815 provides a procedure for calculating the mass oxygen content of fuels using oxygenate concentration in mass percent. When oxygenate concentration in mass percent is not available, the oxygen concentration of these fuels can be determined indirectly by: (1) measuring the volume concentration of the oxygenates in the blend, which may be reported from Test Method D 4815 or equivalent method (2) measuring the density or relative density of the blend, (3) converting the oxygenate concentrations from volume to mass concentrations, and (4) converting the mass oxygenate concentrations to mass oxygen concentrations using the oxygen mass fractions of the oxygenates present.

X4.2 Procedure

X4.2.1 The following steps are used to determine the total mass oxygen concentration of gasoline-oxygenate blends when indirect calculation is necessary.

X4.2.1.1 Determine the volume concentrations of oxygenates in a gasoline-oxygenate blend (Test Method D 4815 or equivalent test method).

X4.2.1.2 Determine the density or relative density of the gasoline-oxygenate blend (Test Methods D 287, D 1298, or D 4052).

X4.2.1.3 The oxygen mass percent of the gasoline-oxygenate blend is calculated using the following general equation. The densities or relative densities and oxygen mass fractions of a number of pure oxygenates are provided in Table X4.1 for use in Eq (X4.1). The choice of density or relative density must be the same as determined in X4.2.1.2 for the gasoline-oxygenate blend.

Oxygen, Mass % =

$$\frac{V_1 \times d_1 \times O_1 + V_2 \times d_2 \times O_2 + \ldots + V_n \times d_n \times O_n}{V_b \times d_b} \times 100 \quad (X4.1)$$

where:
V_n = volume percent of oxygenates 1 through n,
d_n = density or relative density of oxygenates 1 through n,
O_n = mass fraction oxygen in oxygenates 1 through n,
V_b = volume percent of gasoline-oxygenate blend = 100, and
d_b = density or relative density of gasoline-oxygenate blend.

TABLE X4.1 Densities, Relative Densities, and Oxygen Mass Fractions of Pure Oxygenates

Oxygenate	Density, g/mL 20°C (68°F)	Relative Density 15.56/15.56°C (60/60°F)	Oxygen Mass Fraction
Methyl Alcohol	0.7913	0.7983	0.4993
Ethyl Alcohol	0.7894	0.7939	0.3473
n-Propyl Alcohol	0.8038	0.8080	0.2662
Isopropyl Alcohol	0.7855	0.7899	0.2662
n-Butyl Alcohol	0.8097	0.8137	0.2158
Isobutyl Alchol	0.8016	0.8056	0.2158
sec-Butyl Alcohol	0.8069	0.8114	0.2158
tertiary-Butyl Alcohol	0.7866ᴬ	0.7922ᴬ	0.2158
Methyl tertiary-Butyl Ether	0.7406	0.7460	0.1815
Ethyl tertiary-Butyl Ether	0.7399	0.7452	0.1566
tertiary-Amyl Methyl Ether	0.7707	0.7758	0.1566
tertiary-Hexyl Methyl Ether	0.7815	0.7860	0.1377
Diisopropyl Ether	0.7235	0.7282	0.1566

ᴬ Extrapolated, below freezing temperature.

X4.3 Example Calculation

X4.3.1 Assume that a gasoline-oxygenate blend is reported to contain 9.5 volume percent ethanol and 2.0 volume percent methyl tertiary-butyl ether and that the relative density of the blend is measured to be 0.7450, 15.56/15.56°C (60/60°F).

X4.3.2 Using the relative density and oxygen mass fraction data for ethanol and methyl tertiary-butyl ether from Table X4.1, the following mass percent oxygen is calculated for this gasoline-oxygenate blend.

Oxygen, Mass % =

$$\frac{9.5 \times 0.7939 \times 0.3473 + 2.0 \times 0.7460 \times 0.1815}{100 \times 0.7450} \times 100$$

$$= 3.88$$

X4.4 Precision

X4.4.1 The precision of this calculation method is a function of the individual precisions of density or relative density (Test Methods D 287, D 1298, or D 4052) and oxygenate analysis (Test Method D 4815 or equivalent). Because the repeatability and reproducibility vary with the analyses used, no estimate is provided.

Standard Specification for
Automotive Spark-Ignition Engine Fuel[1]

This standard is issued under the fixed designation D 4814; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This specification covers the establishment of requirements of automotive fuels for ground vehicles equipped with spark-ignition engines.

1.2 This specification describes various characteristics of automotive fuels for use over a wide range of operating conditions. It provides for a variation of the volatility and water tolerance of automotive fuel in accordance with seasonal climatic changes at the locality where the fuel is used. For the period May 1 through September 15, the maximum vapor pressure limits issued by the U.S. Environmental Protection Agency (EPA) are specified for each geographical area except Alaska and Hawaii. Variation of the antiknock index with seasonal climatic changes and altitude is discussed in Appendix X1. This specification neither necessarily includes all types of fuels that are satisfactory for automotive vehicles, nor necessarily excludes fuels that can perform unsatisfactorily under certain operating conditions or in certain equipment. The significance of each of the properties of this specification is shown in Appendix X1.

1.3 The spark-ignition engine fuels covered in this specification are gasoline and its blends with oxygenates, such as alcohols and ethers. This specification does not apply to fuels that contain an oxygenate as the primary component, such as Fuel Methanol (M85). The concentrations and types of oxygenates are not specifically limited in this specification. However, depending on oxygenate type, as oxygenate content increases above some threshold level, the likelihood for vehicle problems also increases. The composition of both unleaded and leaded fuel is limited by economic, legal, and technical consideration, but their properties, including volatility, are defined by this specification. In addition, the composition of unleaded fuel is subject to the rules, regulations, and Clean Air Act waivers of the U.S. Environmental Protection Agency (EPA). With regard to fuel properties, including volatility, this specification can be more or less restrictive than the EPA rules,

regulations, and waivers. Refer to Appendix X3 for discussions of EPA rules relating to fuel volatility, lead and phosphorous contents, deposit control additive certification, and use of oxygenates in blends with unleaded gasoline. Contact the EPA for the latest versions of the rules and additional requirements.

1.4 This specification does not address the emission characteristics of reformulated spark-ignition engine fuel. Reformulated spark-ignition engine fuel is required in some areas to lower emissions from automotive vehicles, and its characteristics are described in the research report on reformulated spark-ignition engine fuel.[2] However, in addition to the legal requirements found in this research report, reformulated spark-ignition engine fuel should meet the performance requirements found in this specification.

1.5 This specification represents a description of automotive fuel as of the date of publication. The specification is under continuous review, which can result in revisions based on changes in fuel, automotive requirements, or test methods, or a combination thereof. All users of this specification, therefore, should refer to the latest edition.

NOTE 1—If there is any doubt as to the latest edition of Specification D 4814, contact ASTM International Headquarters.

1.6 Tests applicable to gasoline are not necessarily applicable to its blends with oxygenates. Consequently, the type of fuel under consideration must first be identified in order to select applicable tests. Test Method D 4815 provides a procedure for determining oxygenate concentration in mass percent. Test Method D 4815 also includes procedures for calculating mass oxygen content and oxygenate concentration in volume percent. Appendix X4 provides a procedure for calculating the mass oxygen content of a fuel using measured oxygenate type, oxygenate concentration in volume percent, and measured density or relative density of the fuel.

1.7 The following applies to all specified limits in this standard: For purposes of determining conformance with these specifications, an observed value or a calculated value shall be rounded "to the nearest unit" in the right-most significant digit used in expressing the specification limit, in accordance with

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[1] This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A0 on Gasoline and Oxygenated Fuels.

Current edition approved July 1, 2004. Published August 2004. Originally approved in 1988. Last previous edition approved in 2003 as D 4814–04.

[2] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1347.

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*A Summary of Changes section appears at the end of this standard.

TABLE 1 Vapor Pressure and Distillation Class Requirements

| Vapor Pressure/ Distillation Class | Vapor Pressure,A max, kPa (psi) | Distillation Temperatures, °C (°F), at % Evaporated. maxB | | | | | Distillation Residue, volume % , max | Driveability Index,C max, °C (°F) DerivedD,E |
| | | 10 volume %, max | 50 volume % | | 90 volume %, max | End Point, max | | |
			min	max				
AA	54(7.8)	70.(158.)	77.(170.)	121.(250.)	190.(374.)	225.(437.)	2.	597. (1250.)
A	62(9.0)	70.(158.)	77.(170.)	121.(250.)	190.(374.)	225.(437.)	2.	597. (1250.)
B	69(10.0)	65.(149.)	77.(170.)	118.(245.)	190.(374.)	225.(437.)	2.	591. (1240.)
C	79(11.5)	60.(140.)	77.(170.)	116.(240.)	185.(365.)	225.(437.)	2.	586. (1230.)
D	93(13.5)	55.(131.)	66.(150.)	113.(235.)	185.(365.)	225.(437.)	2.	580. (1220.)
E	103(15.0)	50.(122.)	66.(150.)	110.(230.)	185.(365.)	225.(437.)	2.	569. (1200.)

A Consult EPA for approved test methods for compliance with EPA vapor pressure regulations.

B At 101.3 kPa pressure (760 mm Hg).

C Driveability Index (DI) = $1.5 T_{10} + 3.0 T_{50} + 1.0 T_{90}$, where T_{10} = distillation temperature, °C (°F), at 10 % evaporated, T_{50} = distillation temperature, °C (°F), at 50 % evaporated, and T_{90} = distillation temperature, °C (°F), at 90 % evaporated.

D The DI specification limits are applicable at the refinery or import facility as defined by 40 CFR Part 80.2 and are not subject to correction for precision of the test method.

E Since DI is an index and has no units, the standard temperature conversion from U.S. customary to SI units is not appropriate. The following equation is to be used to make the conversion: $DI_C = (DI_F - 176)/1.8$

the rounding method of Practice E 29. The use of a trailing decimal point in a limit indicates that the digit preceding the decimal point is a significant digit.

1.8 The values stated in SI units are the standard, except when other units are specified by federal regulation. Values given in parentheses are provided for information only.

Note 2—Many of the values shown in Table 1 were originally developed using U.S. customary units and were subsequently soft-converted to SI values. As a result, conversion of the SI values will sometimes differ slightly from the U.S. customary values shown because of round-off. In some cases, federal regulations specify non-SI units.

2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

D 130 Test Method for Corrosiveness to Copper from Petroleum Products by the Copper Strip Test

D 287 Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)

D 381 Test Method for Gum Content in Fuels by Jet Evaporation

D 439 Specification for Automotive Gasoline[4]

D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)

D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)

D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D 2533 Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels

D 2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D 2699 Test Method for Research Octane Number of Spark-Ignition Engine Fuel

D 2700 Test Method for Motor Octane Number of Spark-Ignition Engine Fuel

D 2885 Test Method for Determination of Octane Number of Spark-Ignition Engine Fuels by On-Line Direct Comparison Technique

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D 3231 Test Method for Phosphorus in Gasoline

D 3237 Test Method for Lead in Gasoline by Atomic Absorption Spectrometry

D 3341 Test Method for Lead in Gasoline-Iodine Monochloride Method

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary–Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography

D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)

D 5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy

D 5188 Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)

D 5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method)

D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)

D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Ultraviolet Fluorescence

D 5482 Test Method for Vapor Pressure of Petroleum Products (Mini Method-Atmospheric)

D 5500 Test Method for Vehicle Evaluation of Unleaded Automotive Spark-Ignition Engine Fuel for Intake Valve Deposit Formation

D 5598 Test Method for Evaluating Unleaded Automotive Spark-Ignition Engine Fuel for Electronic Port Fuel Injector Fouling

D 5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective

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[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Withdrawn.

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TABLE 2 Detailed Requirements for All Volatility Classes[A]

Lead Content, max, g/L (g/U.S. gal)[B]		Copper Strip Corrosion, max	Solvent-washed Gum Content, mg/100 mL, max	Sulfur, max, mass %		Oxidation Stability, Minimum, minutes	Water Tolerance
Unleaded	Leaded			Unleaded	Leaded		
0.013(0.05)	1.1(4.2)	No. 1	5	0.0350[C]	0.15	240.	[D]

[A] See Appendix X1 for information on Antiknock Index.

[B] See Appendix X3 for U.S. EPA maximum limits for lead and phosphorus contents in unleaded gasoline (X3.2.1) and maximum average lead limits for leaded gasoline (X3.2.2).

[C] Qualified small refineries have varying maximum sulfur limits up to 0.0450 mass % which are based on their 1997-1998 sulfur level baseline. If values are found in excess of 0.0350 mass %, it is the supplier's responsibility to provide proof that the source was a qualified small refinery.

[D] Water tolerance limits in terms of maximum temperature for phase separation are given in Table 13.

Flame Ionization Detection

D 5845 Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol, and *tert*-Butanol in Gasoline by Infrared Spectroscopy

D 6422 Test Method for Water Tolerance (Phase Separation) of Gasoline-Alcohol Blends

D 6469 Guide for Microbial Contamination in Fuels and Fuel Systems

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

2.2 *Government Standard:*

CFR 40 Code of Federal Regulations[5]

2.3 *Other Standard:*

CCR Title 17, §60100-§60114 California Code of Regulations[6]

3. Terminology

3.1 *Definitions:*

3.1.1 *antiknock index, n*—the arithmetic average of the Research octane number (RON) and Motor octane number (MON), that is, (RON + MON)/2.

3.1.2 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

3.1.3 *gasoline-alcohol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate) of one or more alcohols.

3.1.4 *gasoline-ether blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen) of one or more ethers.

3.1.5 *gasoline-oxygenate blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate) of one or more oxygenates.

3.1.6 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which can be used as a fuel or fuel supplement.

3.1.7 *refinery, n*—a plant at which gasoline or diesel fuel is produced.

3.1.7.1 *Discussion*—This definition is from CFR 40 Part 80.2. In the federal definition, a plant not only covers the conventional refinery, but also covers oxygenate blending and other facilities where gasoline is produced.

3.2 *Applicability*—To determine when a fuel contains a substantial amount of an oxygenate, a gasoline-oxygenate blend is defined as a fuel that contains more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate. The definitions in this section do not apply to fuels that contain an oxygenate as the primary component; for example, fuel methanol (M85).

Note 3—The criteria in 3.2 were selected with consideration given to current oxygenate levels in the marketplace, state labeling practices, and consistency with federal legislation and regulations.

Note 4—Refer to Test Method D 4815 to calculate the mass oxygen content of a fuel using oxygenate concentration in mass %. Refer to Appendix X4 to calculate mass oxygen content of a fuel using oxygenate concentration in volume %.

4. Ordering Information

4.1 The purchasing agency shall:

4.1.1 State the antiknock index as agreed upon with the seller,

4.1.2 Indicate the season and locality in which the fuel is to be used,

4.1.3 Indicate the lead level required (Table 2), and

4.1.4 State the concentration and types of oxygenates present as agreed upon with the seller.

5. Performance Requirements

5.1 Some requirements and test methods applicable to automotive spark-ignition engine fuel depend on whether the fuel is a gasoline, or a gasoline-oxygenate blend. Test Methods D 4815 and D 5599, gas chromatographic test methods, are the recommended procedures to detect the types and amounts of oxygenates. Once the type of fuel is known, the appropriate requirements and test methods can be identified by reference to Table 1, Table 3, and Section 7.

5.2 Volatility of fuels is varied for seasonal climatic changes and conformance to U.S. EPA volatility regulations by providing six vapor pressure/distillation classes and six vapor lock protection classes for fuel. Volatility of fuel is specified by an alphanumeric designation that uses a letter from Table 1 and a number from Table 3.

5.2.1 The seasonal and geographic distribution of the combined vapor pressure/distillation-vapor lock classes is shown in Table 4. Tables 5-7 show the federal ozone nonattainment areas at several vapor lock protection levels that require reduced vapor pressure in the summertime. Tables 8-11 show at several vapor lock protection levels the areas that require federal reformulated spark-ignition engine fuel in the summertime.

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[5] Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

[6] Available from Barclays, 50 California Street, San Francisco, CA 94111.

TABLE 3 Vapor Lock Protection Class Requirements

Vapor Lock Protection Class	Vapor/Liquid Ratio $(V/L)^{A,B}$	
	Test Temperature, °C (°F)	V/L, max
1	60.(140.)	20
2	56.(133.)	20
3	51.(124.)	20
4	47.(116.)	20
5	41.(105.)	20
6	35.(95.)	20

^{A} At 101.3 kPa pressure (760 mm Hg).
^{B} The mercury confining fluid procedure of Test Method D 2533 shall be used for gasoline-oxygenate blends. Either glycerin or mercury confining fluid may be used for gasoline. Test Method D 5188 may be used for all fuels. The procedure for estimating temperature-V/L (see Appendix X2) may only be used for gasoline.

Table 12 shows the areas with restrictive local vapor pressure limits that have been approved under the EPA state implementation plan (SIP).

5.2.2 The EPA vapor pressure regulations can cause the distillation of the fuel to be less volatile, which for some vehicles, results in a worse warm-up driveability performance.

5.2.3 Driveability Index (DI) is intended to provide control of distillation parameters that influence cold start and warm-up driveability. It is a function of the 10 %, 50 %, and 90 % evaporated distillation temperatures measured by Test Method D 86.

5.2.4 Test Method D 2533 contains procedures for measuring temperature-V/L of both gasoline and gasoline-oxygenate blends. For gasoline-oxygenate blends, the procedure requires that mercury be used as the confining fluid in place of glycerin. Either confining fluid may be used for gasoline. Test Method D 5188 is an alternative method for determining vapor-liquid ratio temperatures by an evacuated chamber method for gasoline-oxygenate blends, as well as gasoline. In case of dispute, Test Method D 2533 is the referee method. The method for estimating temperature-V/L (see Appendix X2) is only applicable for gasoline.

5.3 Antiknock index (AKI) is very important to engine performance. The matching of engine octane requirement to fuel octane level (AKI) is critical to the durability and performance of engines; this cannot be accomplished with a single specified minimum level of antiknock index. Appendix X1 includes a discussion of antiknock indexes of fuels currently marketed and relates these levels to the octane needs of broad groups of engines and vehicles. Also discussed is the effect of altitude and weather on vehicle antiknock requirements.

5.4 Additional fuel requirements are shown in Table 2.

5.5 The properties of gasoline-oxygenate blends can differ considerably from those of gasoline. Consequently, additional requirements are needed for gasoline-oxygenate blends. These requirements involve evaluation of compatibility with plastic and elastomeric materials in fuel systems, corrosion of metals, and especially in the case of gasoline-alcohol blends, water tolerance. Requirements for metal corrosion (other than copper) and material compatibility are not given because test methods and appropriate limits are still under development. When these have been developed, they will be included in this specification. Water tolerance is specified in Table 13.

5.6 Depending on oxygenate type and concentration in the blend, vehicle driveability with gasoline-oxygenate blends can differ significantly from that with gasolines having similar volatility characteristics.

5.7 *Water Tolerance*:

5.7.1 The term water tolerance is used to indicate the ability of a gasoline-oxygenate blend to dissolve water without phase separation. This may not be a problem with gasoline-ether blends, but it is of primary concern for alcohol-containing blends, as blends of gasoline with low-molecular weight alcohols generally will dissolve about 0.1 to 0.7 mass % of water under normal conditions, depending on the nature and amount of the alcohol(s) used, the specific hydrocarbons present, and the temperature of the blend. When blends are exposed to a greater amount of water than they can dissolve, they separate into an alcohol-rich aqueous phase, the volume of which can be significantly greater than that of the additional water, and an alcohol-poor hydrocarbon phase. As the aqueous phase can be highly corrosive to many metals and the engine cannot operate on it, such separation is very undesirable. Blends containing low-molecular weight alcohols are generally hygroscopic and can eventually absorb enough moisture from ambient air to cause separation. The problem of phase separation can usually be avoided if the fuels are sufficiently water-free initially and care is taken during distribution to prevent contact with water. To help ensure this, gasoline-alcohol blends shall be tested at the lowest temperatures to which they can be subjected, dependent on the time and place of intended use, as indicated in Table 13. The values in Table 13 are the 10th percentile 6-h minimum temperatures, with each reading specifically defined as the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. For April through September (and occasionally October, and year-round for Hawaii), Table 13 specifies a minimum phase separation temperature of 10°C (50°F), even though the 10th percentile 6-h minimum temperature can be higher. Use of this temperature limit also reduces the risk of separation of the fuel in storage tanks where temperatures may be lower than ambient.

NOTE 5—The values in Table 13 are taken from the U.S. Army Belvoir Research Development and Engineering Center's Report No. 316, entitled "A Predictive Study for Defining Limiting Temperatures and Their

TABLE 4 Schedule of Seasonal and Geographical Volatility Classes[A]

NOTE 1—This schedule, subject to agreement between purchaser and seller, denotes the volatility properties of the fuel at the time and place of bulk delivery to the fuel dispensing facilities for the end user. For Sept. 16 through April 30 (the time period not covered by EPA Phase II vapor pressure requirements), volatility properties for the previous month or the current month are acceptable for the end user from the 1st through the 15th day of the month. From the 16th day through the end of the month, volatility properties of the fuel delivered to the end user shall meet the requirements of the specified class(es). To ensure compliance with EPA Phase II vapor pressure requirements, vapor pressure for finished gasoline tankage at refineries, importers, pipelines, and terminals during May and for the entire distribution system, including retail stations, from June 1 to Sept. 15 shall meet only the current month's class. Shipments should anticipate this schedule.

NOTE 2—Where alternative classes are listed, either class or intermediate classes are acceptable; the option shall be exercised by the seller.

NOTE 3—See Appendix X2 of Research Report: D02-1347[15] for detailed description of areas. Contact EPA for the latest information on areas requiring reformulated fuel.

State	Jan.	Feb.	Mar.	Apr.	May[B]	June	July	Aug.	Sept. 1–15	Sept. 16–30	Oct.	Nov.	Dec.
Alabama	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-2[D]	A-2[D]	A-2/C-3	C-3	C-3/D-4	D-4
Alaska	E-6	E-6	E-6	E-6	E-6/D-4	D-4	D-4	D-4	D-4	D-4/E-6	E-6	E-6	E-6
Arizona:[E]													
N 34° Latitude and E111° Longitude	D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-1	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Remainder of State	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F]	A-1[F]	A-1[D]	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Arkansas	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
California:[E,G]													
North Coast	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[C]	A-2[D]	A-2[D]	A-2[D]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
South Coast	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Southeast	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F,I]	A-1[F,I]	A-1[F,I]	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Interior	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Colorado	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[D]	A-2[D]	A-2[D]	A-2[D]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Connecticut	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/D-4	D-4	D-4/E-5	E-5
Delaware	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
District of Columbia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[K]	A-3[K]	A-3[K]	A-3[K]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Florida	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-3[C]	A-3[C]	A-3/C-3	C-3	C-3/D-4	D-4
Georgia[E]	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-2[D]	A-2[D]	A-2/C-3	C-3	C-3/D-4	D-4
Hawaii	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3
Idaho:													
N 46° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
S 46° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Illinois:[E]													
N 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
S 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4	D-4/E-5
Indiana[E]	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Iowa	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Kansas[E]	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[D]	A-2[D]	A-2[D]	A-2[D]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Kentucky	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Louisiana	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-2[D]	A-2[D]	A-2/C-3	C-3	C-3/D-4	D-4
Maine[E]	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Maryland	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J,K]	A-3[J,K]	A-3[J,K]	A-3[J,K]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Massachusetts	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/D-4	D-4	D-4/E-5	E-5
Michigan[E]	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Minnesota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Mississippi	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-3	A-2	A-2	A-2/C-3	C-3	C-3/D-4	D-4
Missouri[E]	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[C]	A-2[D]	A-2[D]	A-2[D]	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Montana	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Nebraska	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Nevada:													
N 38° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[D]	A-2[D]	A-2[D]	A-2[D]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
S 38° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4
New Hampshire	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/D-4	D-4	D-4/E-5	E-5
New Jersey	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/D-4	D-4	D-4/E-5	E-5
New Mexico:													
N 34° Latitude	E-5/D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
S 34° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4	D-4
New York	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/D-4	D-4	D-4/E-5	E-5
North Carolina	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-2[D]	A-2[D]	A-2/C-3	C-3/D-4	D-4	D-4/E-5
North Dakota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Ohio	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Oklahoma	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Oregon:													
E 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
W 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3[C]	A-3[C]	A-3[C]	A-3[C]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Pennsylvania[E]	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Rhode Island	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3	A-3/D-4	D-4	D-4/E-5	E-5
South Carolina	D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4
South Dakota	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Tennessee	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-2[D]	A-2[D]	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Texas:[E]													

TABLE 4 *Continued*

State	Jan.	Feb.	Mar.	Apr.	May[B]	June	July	Aug.	Sept. 1–15	Sept. 16–30	Oct.	Nov.	Dec.
E 99° Longitude	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C,K]	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2/B-2	B-2/C-3	C- 3/D-4	D-4
W 99° Longitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F]	A-1[F]	A-1[F]	A-1/B-2	B-2/C-3	C-3/D-4	D-4
Utah	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[D]	A-2[D]	A-2[D]	A-2[D]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Vermont	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Virginia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[C,K]	A-3[C,K]	A-3[C,K]	A-3[C,K]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Washington:													
E 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
W 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
West Virginia	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wisconsin	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3[J]	A-3[J]	A-3[J]	A-3[J]	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wyoming	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5

[A] For the period May 1 through September 15, the specified vapor pressure classes comply with 1992 U.S. EPA Phase II volatility regulations. Reformulated spark-ignition engine fuel blended to meet the requirements of the EPA "Complex Model" shall also meet the Phase II volatility regulations. EPA regulations (under the Phase II regulations) allow 1.0 psi higher vapor pressure for gasoline-ethanol blends containing 9 to 10 volume % ethanol for the same period, except for fuels blended to meet the "Complex Model" regulations. See Appendix X3 for additional federal volatility regulations.

[B] Values in parentheses are permitted for retail stations and other end users.

[C] See Table 5 for specific area requirements.

[D] See Table 6 for specific area requirements.

[E] See Table 12 for specific area requirements.

[F] See Table 7 for specific area requirements.

[G] Details of State Climatological Division by CARB air basin and county as indicated (Descriptions of the California Air Basins are found in the California Code of Regulations):

California, North Coast—CARB North Coast, Lake County, San Francisco Bay Area, and North Central Coast Air Basins (Alameda, Contra Costa, Del Norte, Humbolt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, and Trinity Counties and part of Solano County).

California, interior—CARB Northeast Plateau, Sacramento Valley, Mountain Counties, Lake Tahoe, and San Joaquin Valley Air Basins (Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kings, Lassen, Madera, Mariposa, Merced, Modoc, Nevada, Placer, Plumas, Sacramento, San Joaquin, Shasta, Sierra, Siskiyou, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, and Yuba Counties, and parts of Kern and Solano Counties).

California, South Coast—CARB South Central Coast, San Diego, and South Coast Air Basins (Los Angeles, Orange, San Diego, San Luis Obispo, Santa Barbara, and Ventura Counties, and parts of Riverside and San Bernardino Counties).

California, Southeast—CARB Great Basin Valleys, Salton Sea, and Mojave Desert Air Basins (Alpine, Imperial, Inyo, and Mono Counties, and parts of Kern, Los Angeles, Riverside, San Bernardino Counties).

[H] See Table 10 for specific requirements.

[I] See Table 11 for specific area requirements.

[J] See Table 8 for specific area requirements.

[K] See Table 9 for specific area requirements.

TABLE 5 Ozone Nonattainment Areas Requiring Volatility Class AA-3

NOTE—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Alabama[A]—Jefferson and Shelby counties
California[A]—Alameda, Contra Costa, Marin, Monterey, Napa, San Francisco, San Benito, San Mateo, Santa Clara, Santa Cruz, and Solano (part) counties
Florida—Broward, Dade, Duval, Hillsborough, Palm Beach, and Pinellas counties
Georgia[A]—Cherokee, Clayton, Cobb, Coweta, Dekalb, Douglas, Fayette, Forsyth, Fulton, Gwinnett, Henry, Paulding, and Rockdale counties
Louisiana—Ascension, Beauregard, Calcasieu, East Baton Rough, Grant, Iberville, Jefferson, Lafayette, Lafourche, Livingston, Orleans, Point Coupee, Saint Bernard, Saint Charles, Saint James, Saint Mary, and West Baton Rouge parishes
Missouri—Franklin, Jefferson, Saint Charles, and Saint Louis counties; and the city of St. Louis
North Carolina—Davidson, Davie (part), Durham, Forsyth, Gaston, Granville (part), Guilford, Mecklenburgh, and Wake counties
Oregon—Clackamas (part), Marion (part), Multnomah (part), Polk (part), and Washington (part) counties
Tennessee—Davidson, Rutherford, Shelby, Sumner, Williamson, and Wilson counties
Texas—Hardin, Jefferson, Orange, and Victoria counties
Virginia—Smyth County (part)

[A] See Table 12 for local vapor pressure limits.

Application in Petroleum Product Specifications." This can be obtained as Publication AD756-420 from the National Technical Information Service, Springfield, VA 22151.

5.7.2 The water tolerance test procedure consists of cooling gasoline-alcohol blends under specified conditions to the

TABLE 6 Ozone Nonattainment Areas Requiring Volatility Class AA-2

NOTE—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Alabama[A]—Jefferson and Shelby counties
Arizona[A]—Maricopa County
California[A]—Alameda, Butte, Contra Costa, Fresno, Kern (part), Kings, Madera, Marin, Merced, Monterey, Napa, San Benito, San Francisco, San Joaquin, San Mateo, Santa Barbara, Santa Clara, Santa Cruz, Stanislaus, Tulare, and Yuba counties
Colorado—Adams, Arapahoe, Boulder, Denver, Douglas, and Greeley counties
Georgia[A]—Cherokee, Clayton, Cobb, Coweta, Dekalb, Douglas, Fayette, Forsyth, Fulton, Gwinnett, Henry, Paulding, and Rockdale counties
Kansas[A]—Johnson and Wyandotte counties
Louisiana—Ascension, Beauregard, Calcasieu, East Baton Rouge, Grant, Iberville, Jefferson, Lafayette, Lafourche, Livingston, Orleans, Point Coupee, Saint Bernard, Saint Charles, Saint James, Saint Mary, and West Baton Rouge parishes
Missouri—Franklin, Jefferson, Saint Charles, and Saint Louis counties; and the city of St. Louis
Nevada—Washoe County
North Carolina—Davidson, Davie (part), Durham, Forsyth, Gaston, Granville (part), Guilford, Mecklenburgh, and Wake counties
Tennessee—Davidson, Rutherford, Shelby, Sumner, Williamson, and Wilson counties
Texas—Hardin, Jefferson, Orange, and Victoria counties
Utah—Davis and Salt Lake counties

[A] See Table 12 for local vapor pressure limits.

appropriate temperature listed in Table 13. It is important to note that when cooling to a low temperature, some gasoline-alcohol blends can take on a hazy appearance. This haze must

TABLE 7 Ozone Nonattainment Areas Requiring Volatility Class AA-1

Note—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Arizona[A]—Maricopa County
California[A]—Imperial and Kern (part) counties
Texas[A]—El Paso County

[A] See Table 12 for local vapor pressure limits.

TABLE 8 Federal RFG Areas Requiring Volatility Class A-3

Note 1—See 40 CFR Part 81.300 for description of the geographic boundary for each area.
Note 2—No waiver for gasoline-ethanol blends.

Connecticut—All counties
Delaware—All counties
Illinois[A]—Cook, Du Page, Grundy (part), Kane, Kendall (part), Lake, McHenry, and Will counties
Indiana[A]—Lake and Porter counties
Kentucky—Boone, Bullitt (part), Campbell, Jefferson, Kenton, and Oldham (part) counties
Maryland—Cecil County
Massachusetts—All counties
New Hampshire—Hillsborough, Merrimack, Rockingham, and Strafford counties
New Jersey—All counties
New York—Bronx, Dutchess, Essex (part), Kings, Nassau, New York, Orange, Putnam, Queens, Richmond, Rockland, Suffolk, and Westchester counties
Pennsylvania—Bucks, Chester, Delaware, Montgomery, and Philadelphia counties
Rhode Island—All counties
Wisconsin—Kenosha, Milwaukee, Ozaukee, Racine, Washington, and Waukesha counties

[A] See Table 12 for local vapor pressure limits.

TABLE 9 Federal RFG Areas Requiring Volatility Class AA-3

Note 1—See 40 CFR Part 81.300 for description of the geographic boundary for each area.
Note 2—No waiver for gasoline-ethanol blends.

District of Columbia
Maryland—Anne Arundel, Baltimore, Calvert, Carroll, Charles, Frederick, Harford, Howard, Kent, Montgomery, Prince George's, and Queen Anne's counties
Texas—Brazoria, Chambers, Collin, Dallas, Denton, Fort Bend, Galveston, Harris, Liberty, Montgomery, Tarrant, and Waller counties
Virginia—Arlington, Charles City, Chesterfield, Fairfax, Hanover, Henrico, James City, Loudoun, Prince William, Stafford, and York counties and independent cities of Alexandria, Chesapeake, Colonial Heights, Fairfax, Falls Church, Hampton, Hopewell, Manassas, Manassas Park, Newport News, Norfolk, Poquoson, Portsmouth, Richmond, Suffolk, Virginia Beach, and Williamsburg

TABLE 10 Federal RFG Areas Requiring Volatility Class AA-2

Note 1—See 40 CFR Part 81.305 for description of the geographic boundary for each area.
Note 2—No waiver for gasoline-ethanol blends.

California[A]—El Dorado (part), Los Angeles, Orange, Placer (part), Riverside (part), Sacramento, San Bernardino (part), San Diego, Solano (part), Sutter (part), Ventura, and Yolo Counties
Texas—Brazoria, Chambers, Collin, Dallas, Denton, Fort Bend, Galveston, Harris, Liberty, Montgomery, Tarrant, and Waller counties

[A] See Table 12 for local vapor pressure limits.

TABLE 11 Federal RFG Area Requiring Volatility Class AA-1

Note 1—See 40 CFR Part 81.300 for description of the geographic boundary for each area.
Note 2—No waiver for gasoline-ethanol blends.

California[A]—Los Angeles (part), Riverside (part), and San Bernardino (part) counties

[A] See Table 12 for local vapor pressure limits.

accounting to establish that the product was additized at a concentration that was at least equal to the LAC.

6. Workmanship

6.1 The finished fuel shall be visually free of undissolved water, sediment, and suspended matter; it shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

6.2 Fuel to be used in this test shall not be cooled below about 15°C (59°F) or its temperature at the time the sample was taken, whichever is lower, as cooling of gasoline-oxygenate blends can produce changes in appearance that are not reversed on rewarming.

6.3 The finished fuel shall also be free of any adulterant or contaminant that may render the fuel unacceptable for its commonly used applications.

7. Test Methods

7.1 The requirements of this specification shall be determined in accordance with the methods listed below. Refer to the listed test methods to determine applicability or required modifications for use with gasoline-oxygenate blends.

7.1.1 *Distillation*—Test Method D 86.

7.1.2 *Vapor-Liquid Ratio*—Test Method D 2533 has procedures for determining vapor-liquid (*V/L*) ratios for both gasoline and gasoline-oxygenate blends. Because some oxygenates are miscible with the glycerin used in one procedure, another procedure using mercury as the confining fluid is provided for gasoline-oxygenate blends. Either procedure may be used to determine *V/L* for gasoline. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. It may be used for gasoline and gasoline-oxygenate blends.

7.1.3 *Vapor Pressure*—Test Methods D 4953, D 5190, D 5191, or D 5482.

7.1.4 *Corrosion, for Copper*—Test Method D 130, 3 h at 50°C (122°F).

7.1.5 *Solvent-Washed Gum Content*—Test Method D 381, air jet apparatus.

be carefully distinguished from the phase separation test criterion described in Test Method D 6422 and must not be considered grounds for rejection of the fuel. This test must not be confused with that described in Section 6, which is conducted at 21°C (70°F) or above, and for which the appearance of haze is proper grounds for rejection.

5.8 Deposit control additives are added to fuel to help keep carburetors, fuel injectors, and intake valves clean. Deposit control additives are required to be certified by the EPA as summarized in X3.5. Each additive is certified for use at a lowest additive concentration (LAC), which is the lowest level certified to be effective in preventing deposit formation. All parties who blend deposit control additives into fuel must complete mandatory volume additive reconciliation (VAR)

TABLE 12 Federal Approved State Implementation Plan Areas Requiring More Restrictive Maximum Vapor Pressure Limits

NOTE—Some areas are awaiting official EPA approval for the more restrictive local vapor pressure limits.

Alabama—Jefferson and Shelby counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15
Arizona—Maricopa County—48.2 kPa (7.0 psi) max May 31 - Sept. 30, 62.0 kPa (9.0 psi) max Oct. 1 - Mar. 31
California—48.26 kPa (7.00 psi) max April 1, May 1, or June 1 - Sept. 30 or Oct. 31 depending on air basin
Georgia—Banks, Barrow, Bartow, Butts, Carroll, Chatooga, Cherokee, Clarke, Clayton, Cobb, Coweta, Dawson, Dekalb, Douglas, Fayette, Floyd, Forsyth, Fulton, Gwinnett, Hall, Haralson, Heard, Henry, Jackson, Jasper, Jones, Lamar, Lumpkin, Madision, Meriwether, Monroe, Morgan, Newton, Oconee, Paulding, Pickens, Pike, Polk, Putnam, Rockdale, Spalding, Troup, Upson, and Walton counties—48.2 kPa (7.0 psi) max June 1 - Sept 15[A]
Illinois—Madison, Monroe, and Saint Clair Counties area – 49.6 kPa (7.2 psi) max June 1 - Sept. 15[A]
Indiana—Clark and Floyd counties area – 53.8 kPa (7.8 psi) max May 1 terminal/June 1 retail - Sept. 15[A]
Kansas—Johnson and Wyandotte counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15[A]
Maine—Androscoggin, Cumberland, Kennebec, Knox, Lincoln, Sagadahoc, and York Counties—53.8 kPa (7.8 psi) max May 1-Sept 15
Michigan—Livingston, Macomb, Monroe, Oakland, Saint Clair, Washtenaw, and Wayne counties—53.8 kPa (7.8 psi) max June 1 - Sept 15
Missouri—Clay, Jackson, and Platte counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15[A]
Pennsylvania—Allegheny, Armstrong, Beaver, Butler, Fayette, Washington, and Westmoreland counties—53.8 kPa (7.8 psi) max June 1 - Sept. 15
Texas—El Paso County—48.2 kPa (7.0 psi) max May 1 terminal/June 1 retail - Sept. 15
Texas—Anderson, Angelina, Aransas, Atascosa, Austin, Bastrop, Bee, Bell, Bexar, Bosque, Bowie, Brazos, Burleson, Caldwell, Calhoun, Camp, Cass, Cherokee, Colorado, Comal, Cooke, Coryell, De Witt, Delta, Ellis, Falls, Fannin, Fayette, Franklin, Freestone, Goliad, Gonzales, Grayson, Gregg, Grimes, Guadalupe, Harrison, Hays, Henderson, Hill, Hood, Hopkins, Houston, Hunt, Jackson, Jasper, Johnson, Karnes, Kaufman, Lamar, Lavaca, Lee, Leon, Limestone, Live Oak, Madison, Marion, Matagorda, McLennan, Milam, Morris, Nacogdoches, Nararro, Newton, Nueces, Panola, Parker, Polk, Rains, Red River, Refugio, Robertson, Rockwall, Rusk, Sabine, San Jacinto, San Patricio, San Augustine, Shelby, Smith, Somervell, Titus, Travis, Trinity, Tyler, Upshur, Van-Zandt, Victoria, Walker, Washington, Wharton, Williamson, Wilson, Wise, and Wood counties—53.8 kPa (7.8 psi) max May 1 terminal/June 1 retail - October 1

[A] A 1.0 psi higher vapor pressure is allowed for gasoline-ethanol blends containing 9 to 10 volume % ethanol.

7.1.6 *Sulfur*—Test Methods D 1266, D 2622, D 3120, or D 5453. With Test Method D 3120, fuels with sulfur content greater than 100 ppm (0.0100 mass %) must be diluted with *iso*octane. The dilution of the sample may result in a loss of precision. Test Method D 3120 cannot be used when the lead concentration is greater than 0.4 g/L (1.4 g/U.S. gal).

7.1.7 *Lead*—Test Methods D 3341 or D 5059 (Test Methods A or B). For lead levels below 0.03 g/L (0.1 g/U.S. gal), use Test Methods D 3237 or D 5059 (Test Method C).

7.1.8 *Oxidation Stability*—Test Method D 525.

7.1.9 *Oxygenate Detection*—Test Methods D 4815, D 5599, or D 5845. These test methods are designed for the quantitative determination of methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), methyl alcohol, ethyl alcohol, and *tert*-butyl alcohol. In addition, Test Methods D 4815 and D 5599 are designed for the quantitative determination of *n*-propyl alcohol, *iso*propyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol *iso*butyl alcohol, and *tert*-pentyl alcohol. Results for all of these test methods are reported in mass %. Test Method D 4815

includes procedures for calculating oxygenate concentration in volume % and mass oxygen content using the mass % oxygenate results.

7.1.10 *Water Tolerance*—See Test Method D 6422.

8. Precision and Bias [7]

8.1 The precision of each required test method for the properties specified is included in the standard applicable to each method, with the exception of Driveability Index. In many cases, the precision applicable to gasoline-oxygenate blends has not been established yet.

8.2 *Precision and Bias of Driveability Index (DI)*:

8.2.1 The following statements apply to the precision and bias of DI, which is a derived quantity not addressed in any other standard.[7]

8.2.2 The precision of DI is a function of the individual precisions of the 10 %, 50 %, and 90 % evaporated temperatures from Test Method D 86. The precisions of these percent evaporated temperatures vary for different apparatuses (manual or automatic), for fuels of different volatilities (for example, above and below 65.5 kPa (9.5 psi) vapor pressure) and with different distillation curve slopes.

8.2.3 *Repeatability*—The difference between two successive DI determinations using Test Method D 86 results, where the two test results were obtained by one operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in normal and correct operation of the test method, exceed 9°C (17°F) derived units in only one case in twenty.

8.2.4 The repeatability value was calculated using the precision data from Test Method D 86 and average distillation characteristics from the 1994 through 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Motor Gasoline and from the 1997 and 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Reformulated Gasoline.

8.2.5 *Reproducibility*—The difference between two single and independent DI determinations using Test Method D 86 results, where the two test results were obtained by different operators in different laboratories on identical test material, would in the long run, in normal and correct operation of the test method, exceed 27°C (48°F) derived units in only one case in twenty.

8.2.6 The reproducibility values were determined directly using the distillation data from each laboratory participating in cooperative programs to calculate DI. The data used to calculate DI were available from the 1994 through 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Motor Gasoline, the 1997 and 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Reformulated Gasoline, the Auto/Oil Air Quality Improvement Research Program, the Auto/Oil AAMA Gasoline Inspections Program, and the 1995 to 1996 CRC volatility program.

8.2.7 *Bias*—Since there is no acceptable reference material suitable for determining bias for DI, bias has not been determined.

[7] Supporting data (calculations) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1468.

TABLE 13 Maximum Temperature for Phase Separation, °C[A]

State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
						Temperature Conversion °F = (°C × 1.8) + 32°						
Alabama	-4.	-3.	0.	5.	10.	10.	10.	10.	10.	6.	0.	-4.
[B] Alaska:												
Southern Region	-27.	-26.	-23.	-11.	1.	7.	9.	7.	1.	-9.	-19.	-23.
South Mainland N of 62° Latitude	-41.	-39.	-31.	-14.	-1.	7.	9.	5.	-2.	-18.	-32.	-41.
Arizona:												
N of 34° Latitude	-11.	-7.	-7.	-2.	2.	6.	10.	10.	6.	1.	-6.	-9.
S of 34° Latitude	-2.	-1.	2.	-7.	10.	10.	10.	10.	10.	9.	2.	-1.
Arkansas	-9.	-6.	-2.	6.	10.	10.	10.	10.	10.	4.	-2.	-6.
[C] California												
North Coast	-2.	0.	1.	4.	5.	8.	9.	9.	8.	6.	2.	-2.
South Coast	-2.	-1.	2.	4.	7.	9.	10.	10.	9.	6.	1.	-2.
Southeast	-7.	-3.	-1.	3.	8.	10.	10.	10.	9.	4.	-3.	-6.
Interior	-4.	-3.	-3.	-1.	3.	9.	10.	10.	10.	6.	0.	-2.
Colorado:												
E of 105° Longitude	-14.	-12.	-9.	-3.	4.	10.	10.	10.	7.	1.	-8.	-11.
W of 105° Longitude	-24.	-20.	-12.	-6.	-1.	4.	8.	6.	1.	-6.	-14.	-21.
Connecticut	-14.	-13.	-8.	-1.	5.	10.	10.	10.	7.	1.	-4.	-12.
Delaware	-9.	-8.	-3.	0.	8.	10.	10.	10.	10.	4.	-1.	-8.
District Columbia	-8.	-7.	-3.	3.	9.	10.	10.	10.	10.	5.	0.	-7.
Florida:												
N of 29° Latitude	-1.	1.	4.	9.	10.	10.	10.	10.	10.	9.	3.	-1.
S of 29° Latitude	4.	7.	8.	10.	10.	10.	10.	10.	10.	10.	9.	5.
Georgia	-5.	-2.	1.	6.	10.	10.	10.	10.	10.	6.	0.	-3.
Hawaii	10.	10.	10.	10.	10.	10.	10.	10.	10.	10.	10.	10.
Idaho	-17.	-16.	-11.	-3.	-5.	4.	10.	9.	3.	-2.	-11.	-15.
Illinois:												
N of 40° Latitude	-18.	-16.	-9.	-1.	4.	10.	10.	10.	7.	1.	-7.	-16.
S of 40° Latitude	-15.	-12.	-7.	1.	7.	10.	10.	10.	9.	3.	-6.	-13.
Indiana	-16.	-13.	-7.	-1.	4.	10.	10.	10.	7.	1.	-6.	-14.
Iowa	-23.	-19.	-13.	-3.	4.	10.	10.	10.	6.	0.	-12.	-20.
Kansas	-17.	-12.	-9.	-3.	5.	10.	10.	10.	7.	0.	-8.	-13.
Kentucky	-12.	-9.	-4.	1.	8.	10.	10.	10.	9.	3.	-4.	-11.
Louisiana	-3.	0.	3.	8.	10.	10.	10.	10.	10.	7.	2.	-1.
Maine	-24.	-22.	-16.	-4.	1.	7.	10.	8.	3.	-2.	-8.	-20.
Maryland	-9.	-8.	-3.	3.	9.	10.	10.	10.	10.	4.	-2.	-8.
Massachusetts	-15.	-14.	-7.	-1.	4.	10.	10.	10.	6.	0.	-4.	-13.
[D] Michigan:												
Lower Michigan	-18.	-17.	-12.	-3.	1.	7.	10.	9.	5.	0.	-6.	-14.
Upper Michigan	-21.	-20.	-15.	-6.	-1.	6.	9.	9.	4.	-1.	-9.	-18.
Minnesota	-31.	-28.	-20.	-7.	0.	6.	10.	8.	1.	-3.	-16.	-28.
Mississippi	-3.	-1.	2.	7.	10.	10.	10.	10.	10.	7.	1.	-3.
Missouri	-14.	-11.	-6.	1.	8.	10.	10.	10.	10.	3.	-5.	-12.
Montana	-28.	-24.	-19.	-6.	1.	5.	9.	8.	1.	-5.	-17.	-23.
Nebraska	-19.	-14.	-11.	-3.	4.	9.	10.	10.	5.	-2.	-10.	-16.
Nevada:												
N of 38° Latitude	-18.	-13.	-8.	-3.	1.	5.	9.	7.	2.	-3.	-11.	-14.
S of 38° Latitude	-9.	-5.	-1.	1.	9.	10.	10.	10.	10.	4.	-3.	-6.
New Hampshire	-18.	-17.	-9.	-2.	3.	9.	10.	9.	3.	-1.	-6.	-16.
New Jersey	-10.	-9.	-4.	2.	7.	10.	10.	10.	10.	4.	-1.	-8.
New Mexico:												
N of 34° Latitude	-14.	-11.	-7.	-2.	1.	7.	10.	10.	7.	1.	-8.	-12.
S of 34° Latitude	-7.	-5.	-1.	6.	10.	10.	10.	10.	10.	7.	-2.	-5.
New York:												
N of 42° Latitude	-21.	-20.	-13.	-3.	2.	9.	10.	10.	4.	-1.	-6.	-18.
S of 42° Latitude	-13.	-13.	-7.	1.	6.	10.	10.	10.	8.	2.	-3.	-12.
North Carolina	-9.	-7.	-3.	1.	7.	10.	10.	10.	8.	1.	-5.	-8.
North Dakota	-29.	-27.	-11.	-6.	1.	8.	10.	10.	3.	-2.	-17.	-24.
Ohio	-14.	-13.	-8.	-2.	6.	10.	10.	10.	7.	1.	-5.	-13.
Oklahoma	-12.	-6.	-5.	1.	7.	10.	10.	10.	10.	4.	-4.	-9.
Oregon:												
E of 122° Longitude	-17.	-12.	-6.	-3.	0.	4.	6.	6.	2.	-3.	-8.	-12.
W of 122° Longitude	-5.	-3.	-1.	2.	5.	8.	10.	10.	7.	2.	-3.	-3.
Pennsylvania:												
N of 41° Latitude	-17.	-19.	-13.	-4.	1.	6.	9.	8.	2.	-1.	-6.	-16.
S of 41° Latitude	-13.	-14.	-9.	-1.	5.	10.	10.	10.	7.	2.	-4.	-12.
Rhode Island	-11.	-11.	-5.	1.	6.	10.	10.	10.	8.	3.	-2.	-10.
South Carolina	-3.	-2.	0.	6.	10.	10.	10.	10.	10.	7.	1.	-3.
South Dakota	-24.	-21.	-16.	-4.	3.	10.	10.	10.	4.	-2.	-12.	-21.
Tennessee	-9.	-7.	-3.	2.	9.	10.	10.	10.	10.	2.	-3.	-8.
Texas:												
N of 31° Latitude	-11.	-8.	-4.	2.	8.	10.	10.	10.	10.	5.	-3.	-7.

TABLE 13 *Continued*

State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
S of 31° Latitude	-1.	1.	4.	10.	10.	10.	10.	10.	10.	10.	3.	1.
Utah	-15.	-11.	-7.	-2.	2.	8.	10.	10.	7.	2.	-11.	-12.
Vermont	-20.	-21.	-12.	-2.	2.	9.	10.	10.	5.	0.	-6.	-17.
Virginia	-8.	-7.	-3.	3.	9.	10.	10.	10.	10.	4.	-2.	-7.
Washington:												
E of 122° Longitude	-13.	-6.	-3.	1.	4.	7.	10.	10.	7.	1.	-5.	-7.
W of 122° Longitude	-6.	-2.	-2.	1.	4.	7.	9.	9.	6.	2.	-2.	-2.
West Virginia	-13.	-12.	-7.	-2.	4.	9.	10.	10.	5.	-2.	-7.	-12.
Wisconsin	-25.	-21.	-15.	-3.	3.	8.	10.	10.	5.	-1.	-11.	-21.
Wyoming	-23.	-17.	-14.	-6.	0.	5.	10.	10.	3.	-2.	-13.	-16.

Temperature Conversion °F = (°C × 1.8) + 32°

[A] A maximum phase separation temperature of 10°C (50°F) is specified, even if the 6-h 10th percentile minimum temperature for the area and month can be higher.

[B] The designated areas of Alaska are divided as follows: *Southern Region*—The Aleutians, Kodiak Island, the coastal strip East of Longitude 141°, and the Alaskan Peninsula South of Latitude 52°.

South Mainland—The portion of Alaska South of Latitude 62°, except the Southern Region.

North of Latitude 62°—The specification test temperature must be agreed between the vendor and purchaser having regard to equipment design, expected weather conditions, and other relevant factors.

[C] The designated areas of California are divided by county as follows: *North Coast*—Alameda, Contra Costa, Del Norte, Humbolt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity.

Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (excepting that portion lying east of the Los Angles County Aqueduct, Kings, Madera, Mariposa, Merced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada.

South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct).

Southeast—Imperial, Riverside, San Bernardino, Los Angeles (that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct).

[D] The designated areas of Michigan are divided as follows: *Lower Michigan*—That portion of the state lying East of Lake Michigan.

Upper Michigan—That portion of the state lying North of Wisconsin and of Lake Michigan.

9. Keywords

9.1 alcohol; antiknock index; automotive fuel; automotive gasoline; automotive spark-ignition engine fuel; copper strip corrosion; corrosion; distillation; driveability; Driveability Index; EPA regulations; ethanol; ether; fuel; gasoline; gasoline-alcohol blend; gasoline-ethanol blend; gasoline-ether blend; gasoline-oxygenate blend; induction period; lead; leaded fuel; methanol; MTBE; octane number; octane requirement; oxidation stability; oxygenate; oxygenate detection; phase separation; phosphorous; solvent-washed gum; sulfur; $T_{V/L} = 20$; unleaded fuel; vapor-liquid ratio; vapor lock; vapor pressure; volatility; water tolerance

APPENDIXES

(Nonmandatory Information)

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR AUTOMOTIVE SPARK-IGNITION ENGINE FUEL

X1.1 General

X1.1.1 Antiknock rating and volatility define the general characteristics of automotive spark-ignition engine fuel. Other characteristics relate to the following: limiting the concentration of undesirable components so that they will not adversely affect engine performance and ensuring the stability of fuel as well as its compatibility with materials used in engines and their fuel systems.

X1.1.2 Fuel for spark-ignition engines is a complex mixture composed of relatively volatile hydrocarbons that vary widely in their physical and chemical properties and may contain oxygenates. Fuel is exposed to a wide variety of mechanical, physical, and chemical environments. Thus, the properties of fuel must be balanced to give satisfactory engine performance over an extremely wide range of operating conditions. The prevailing standards for fuel represent compromises among the numerous quality and performance requirements. This ASTM specification is established on the basis of the broad experience and close cooperation of producers of fuel, manufacturers of automotive equipment, and users of both.

X1.2 Engine Knock

X1.2.1 The fuel-air mixture in the cylinder of a spark-ignition engine will, under certain conditions, autoignite in localized areas ahead of the flame front that is progressing from the spark. This is engine spark knock which can cause a ping that may be audible to the customer.

X1.2.2 The antiknock rating of a fuel is a measure of its resistance to knock. The antiknock requirement of an engine depends on engine design and operation, as well as atmospheric conditions. Fuel with an antiknock rating higher than that required for knock-free operation does not improve performance.

X1.2.3 A decrease in antiknock rating may cause vehicle performance loss. However, vehicles equipped with knock limiters can show a performance improvement as the antiknock

quality of the fuel is increased in the range between customer-audible knock and knock-free operation. The loss of power and the damage to an automotive engine due to knocking are generally not significant until the knock intensity becomes very severe. Heavy and prolonged knocking may cause power loss and damage to the engine.

X1.3 Laboratory Octane Number

X1.3.1 The two recognized laboratory engine test methods for determining the antiknock rating of fuels are the Research method (Test Methods D 2699 or D 2885) and the Motor method (Test Methods D 2700 or D 2885). The following paragraphs define the two methods and describe their significance as applied to various equipment and operating conditions.

X1.3.2 Research octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under mild operating conditions; namely, at a moderate inlet mixture temperature and a low engine speed. Research octane number tends to indicate fuel antiknock performance in engines at wide-open throttle and low-to-medium engine speeds.

X1.3.3 Motor octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under more severe operating conditions than those employed in the Research method; namely, at a higher inlet mixture temperature and at a higher engine speed. It indicates fuel antiknock performance in engines operating at wide-open throttle and high engine speeds. Also, Motor octane number tends to indicate fuel antiknock performance under part-throttle, road-load conditions.

X1.4 Road Octane Number

X1.4.1 The road octane of a fuel is the measure of its ability to resist knock in customers' vehicles, and is ultimately of more importance than laboratory octane numbers. Since road octanes are difficult to measure and interpret, the industry has agreed to use ASTM laboratory engine tests to estimate the road octane performance of spark-ignition engine fuel in vehicles.

X1.4.2 The antiknock index (AKI) is the arithmetic average of the Research octane number (RON) and Motor octane number (MON):

$$AKI = (RON + MON)/2 \qquad (X1.1)$$

This value is called by a variety of names, in addition to antiknock index, including:

Octane rating
Posted octane
(R + M)/2 octane

X1.4.3 The AKI is posted on retail gasoline dispensing pumps in the United States and is referred to in car owners' manuals. The AKI is also required for certification at each wholesale fuel transfer and is referred to in United States federal law as "Octane Rating."[8]

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[8] Details of this regulation can be found in Code of Federal Regulations Title 16, Chapter 1, Subchapter C, part 306 (16 CFR306), U.S. Government Printing Office, Superintendent of Documents, Washington DC 20402.

FIG. X1.1 An Example of the Statistical Distribution of Vehicle Antiknock Requirements

X1.4.4 The most extensive data base that relates the laboratory engine test methods for Research and Motor octane to actual field performance of fuel in vehicles is the annual Coordinating Research Council (CRC)[9] Octane Number Requirement Survey conducted for new light-duty vehicles. Analysis of these data shows that the antiknock performance of a fuel in some vehicles may correlate best with Research octane number, while in others, it may correlate best with Motor octane number. These correlations also differ from model year to model year or from vehicle population to vehicle population, reflecting changes in engine designs over the years.

X1.4.5 The antiknock index of a fuel approximates the CRC road octane ratings for many vehicles. However, the user must also be guided by experience as to which fuel is most appropriate for an individual vehicle. The antiknock index formula is reviewed periodically and may have to be adjusted in the future as engines and fuels continue to evolve. The present (RON + MON)/2 formula is an estimate and is not an absolute measure of fuel antiknock performance in general or in any specific vehicle.

X1.4.6 Car antiknock requirements vary, even within a single model, so the statistical distribution of the octane needs of any car population are usually shown in graphical form, as shown in Fig. X1.1. As antiknock index increases, larger and larger fractions of the car population in question will be free of

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[9] Coordinating Research Council, Inc., 3650 Mansell Rd., Ste. 140, Alpharetta, GA 30022–8246.

TABLE X1.1 Automotive Spark-Ignition Engine Fuel Antiknock Indexes in Current Practice

Unleaded Fuel[A] (for vehicles that can or must use unleaded fuel)	
Antiknock Index[B,C,D,E] (RON + MON)/2	Application
87	Designed to meet antiknock requirements of most 1971 and later model vehicles
89	Satisfies vehicles with somewhat higher antiknock requirements
91 and above	Satisfies vehicles with high antiknock requirements
Leaded Fuel (for vehicles that can or must use leaded fuel)	
Antiknock Index[B,C,D,E] (RON + MON)/2	Application
88	For most vehicles that were designed to operate on leaded fuel

[A] Unleaded fuel having an antiknock index of at least 87 should also have a minimum Motor octane number of 82 in order to adequately protect those vehicles that are sensitive to Motor octane quality.

[B] Reductions in vehicle antiknock requirements for altitude are shown in Fig. X1.2.

[C] Reductions in vehicle antiknock requirements for seasonal variations are shown in Fig. X1.3.

[D] Not all antiknock index levels listed in this table are available at all locations.

[E] The Federal Trade Commission requires octane posting and certification in accordance with 16 CFR Part 306.

knock, that is, be "satisfied" with the octane quality of fuels at or above that level of antiknock index. The data in Fig. X1.1 are for new model cars and trucks sold in the United States in the model year 1988 and are included as an example of the antiknock requirement distribution, not as a data reference.

X1.4.7 According to the winter 1988–1989 motor gasoline survey published by the National Institute for Petroleum and Energy Research, unleaded fuel antiknock indexes in current practice range from a low near 84 in the mountain areas to a high of near 94. Companies typically market two or three unleaded grades of fuel, one of which usually has a minimum antiknock index of 87, for which most post-1971 vehicles are designed. Most companies also market a higher octane fuel with an antiknock index of 91 or above. This fuel is intended to satisfy those vehicles with a higher octane requirement. Some companies offer three grades of unleaded fuel. The third grade usually has an antiknock index of 89. Leaded fuel is still available in some markets and usually has an antiknock index of 88 or 89.

X1.4.8 Marketers set the grades and octane based on their perception of the technical and competitive needs in the market.

X1.4.9 Antiknock indexes of fuel sold in current practice in the United States are shown in Table X1.1 for both unleaded and leaded fuels.

X1.5 Precision and Bias of Antiknock Index

X1.5.1 The following statements apply to the precision and bias of antiknock index of fuel, which is a composite quantity not addressed in any other standard.

X1.5.2 The precision of the antiknock index, (RON + MON)/2, is a function of the individual precisions of Research (Test Method D 2699) and Motor (Test Method D 2700) octane numbers. The repeatability and reproducibility variances for these test methods are summed and divided by four to obtain the variance of the antiknock index.

X1.5.2.1 *Repeatability*—The difference between two sets of antiknock index determinations, where two test results by each octane number method were obtained by one operator, with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

X1.5.2.2 *Reproducibility*—The difference between two independent sets of antiknock index determinations, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

Antiknock Index	Repeatability, Antiknock Index Units	Reproducibility, Antiknock Index Units
83	0.2	0.7
85	0.2	0.7
87	0.2	0.6
89	0.2	0.6
91	0.2	0.6
93	0.2	0.6
95	—	0.6
97	—	0.7

NOTE X1.1—These precision values were calculated from Research and Motor octane number results utilizing exchange sample test data obtained by the ASTM National Exchange Group (NEG), the Institute of Petroleum, or the Institut Français du Petrole, or combination thereof, participating in cooperative testing programs. The precision values for 83, 85, 95, and 97 AKI were obtained from NEG data during the period 1980 through 1982 and have been analyzed in accordance with RR: D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants," Spring 1973.[10] The precision values for 87 though 93 AKI were calculated using the data from RR: D02-1383, "Research and Motor Octane Number Precision Study Report, 1988 through 1994," December 1995.[11]

X1.5.2.3 *Bias*—Since knock ratings are determined by the conditions of the empirical test methods involved, bias cannot be determined.

X1.6 Effects of Altitude and Weather on Vehicle Antiknock Requirement

X1.6.1 A vehicle's antiknock requirement can vary with changes in altitude, ambient temperature, and humidity, depending on the control system of the vehicle. New vehicles have sensors to measure and engine management computers, which take into account such conditions as air charge temperature and barometric pressure. These vehicles are designed to have the same antiknock requirement at all altitudes and a reduced sensitivity to changes in ambient temperature. This more sophisticated control technology began to be used extensively in 1984. This technology, while constantly evolving and improving, is used on almost all new vehicles. This means that many vehicles in today's fleet require fuel having the same antiknock index regardless of changes in altitude or ambient temperatures. Older vehicles, which do not have sophisticated control systems, will likely experience changes in antiknock

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[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1007.

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1383.
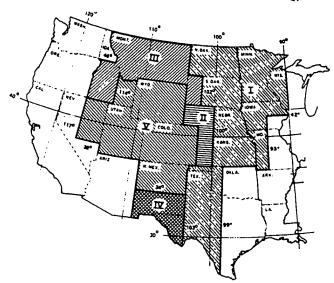
FIG. X1.2 Reduction in Vehicle Antiknock Requirements for Altitude[A,B]

Area	Less than 89 AKI	89 AKI or Greater[A,B]
I	0.7	0.5
II	1.5	1.5
III	2.2	1.5
IV	3.0	2.0
V	4.5	3.0

[A] Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

[B] While the reductions in this table apply to most pre-1984 vehicles, the control technology on almost all new vehicles will cause them to have no reduction in antiknock requirement at higher altitudes.

requirement due to changes in altitude and weather conditions. However, the changes in antiknock requirement indicated in the following sections apply to a continually smaller part of the vehicle fleet.

X1.6.2 The antiknock requirement of an older vehicle decreases as altitude increases, primarily due to reduction in mixture density caused by reduced atmospheric pressure. The change in antiknock requirement for altitude for older vehicles is given in Fig. X1.2. Boundaries of the areas defined and the corresponding antiknock index reductions were established to protect vehicles driven from a higher altitude to a lower altitude (and, hence higher antiknock requirement) area while using a fuel obtained in the high altitude area.

X1.6.3 Tests by CRC and other organizations have shown that the decrease in antiknock requirements with altitude is larger for most models between 1971 and 1984, designed to use a fuel with an antiknock index of 87, than for pre-1971 vehicles. Generally the pre-1971 vehicles have high compression ratios and were designed for fuels with an antiknock index of 88 or higher. Fuels with antiknock indexes below 89 are adjusted by a larger factor than those with an antiknock index of 89 or greater.

X1.6.4 The antiknock requirements of older vehicles rise with increasing ambient temperature on the average by 0.097 MON per degree Celsius (0.054 MON per degree Fahrenheit).

X1.6.5 The antiknock requirements of both older and new vehicles decrease with increasing specific humidity by 0.245

FIG. X1.3 Reduction in Vehicle Antiknock Requirements for Weather[A]

	J	F	M	A	M	J	J	A	S	O	N	D
Northeast	1.0	0.5	0.5	0	0	0	0	0	0	0.5	0.5	1.0
Southeast	0.5	0	0	0	0	0.5	0.5	0.5	0.5	0	0	0.5
Midwest	1.0	0.5	0.5	0	0	0	0	0	0	0	0.5	1.0
Northwest	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Southwest	1.0	0.5	0	0	0	0	0	0	0	0	0.5	1.0
California[A,B]												
No Coast	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0.5	0.5
So Coast	0	0	0.5	0.5	1.0	1.0	1.0	0.5	0.5	0	0	0
Alaska	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Hawaii	0	0	0	0	0	0	0	0	0	0	0	0

[A] Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

[B] Details of California coastal areas are shown in Footnote G of Table 4.

MON per gram of water per kilogram of dry air (0.035 MON per grain of water per pound of dry air).

X1.6.6 Because temperature and humidity of geographical areas are predictable throughout the year from past weather records, antiknock index levels can be adjusted to match seasonal changes in vehicle antiknock requirements. Fig. X1.3 defines the boundaries of areas and the typical reduction in vehicle antiknock requirements for weather for older vehicles. This figure may not apply to newer vehicles.

X1.7 Leaded Versus Unleaded Fuel Needs

X1.7.1 In addition to selecting the appropriate antiknock index to meet vehicle antiknock needs, a choice must be made between leaded and unleaded fuel. Vehicles that must use unleaded fuel are required by Environmental Protection Agency regulation to have permanent labels on the instrument panel and adjacent to the fuel tank filler inlet reading "Unleaded Fuel Only." Most 1975 and later model passenger cars and light trucks are in this category. Most 1971-1974 vehicles can use leaded or unleaded fuel. Pre-1971 vehicles were designed for leaded fuel; however, unleaded fuel of suitable antiknock index may generally be used in these vehicles, except that leaded fuel should be used periodically (after a few tankfuls of unleaded fuel have been used). Leaded fuel may be required in some vehicles, particularly trucks, in heavy-duty service and some farm equipment. Instructions on fuel selection are normally provided in publications of vehicles manufacturers (for example, owner's manuals, service bulletins, and so forth). Antiknock agents other than lead alkyls may be used to increase the antiknock index of fuels, and their concentrations may also be limited due to either performance or legal requirements.

X1.8 Volatility

X1.8.1 In most spark-ignition internal combustion engines, the fuel is metered in liquid form through the carburetor or fuel injector, and is mixed with air and partially vaporized before entering the cylinders of the engine. Consequently, volatility is an extremely important characteristic of motor fuel.

X1.8.2 At high operating temperatures, fuels can boil in fuel pumps, lines, or carburetors. If too much vapor is formed, the fuel flow to the engine can be decreased, resulting in loss of power, rough engine operation, or engine stoppage. These conditions are known as "vapor lock." Conversely, fuels that do not vaporize sufficiently can cause hard starting of cold engines and poor warm-up performance. These conditions can be minimized by proper selection of volatility requirements, but cannot always be avoided. For example, during spring and fall, a fuel of volatility suitable for satisfactory starting at low ambient temperatures can cause problems in some engines under higher ambient temperature operating conditions.

X1.8.3 Six vapor pressure/distillation classes and six vapor lock protection (vapor-liquid ratio) classes of fuel are provided to satisfy vehicle performance requirements under different climatic conditions and to comply with U.S. EPA vapor pressure limits for the control period of May 1 through September 15. Class A and Class AA specify the EPA maximum vapor pressure limits of 9.0 psi and 7.8 psi, respectively. Volatility of fuel is specified by an alphanumeric designation. The letter specifies the vapor pressure/distillation class and the number specifies the vapor lock protection class. The vapor pressure/distillation classes are needed to comply with the EPA vapor pressure regulations and are not based on vehicle performance during the EPA control period. The separate vapor lock protection classes are provided because under most ambient conditions, the EPA regulations specify a lower vapor pressure than would be required to prevent hot fuel handling problems. If the corresponding and unnecessarily more restrictive vapor-liquid ratios were specified when the EPA regulations are in effect, it could result in reduced fuel production, manufacturing hardships, and increased fuel costs. The schedule for seasonal and geographical distribution indicates the appropriate alphanumeric volatility requirement or requirements for each month in all areas of the United States, based on altitude and expected air temperatures, and on EPA vapor pressure regulations. Volatility limits are established in terms of vapor-liquid ratio, vapor pressure, and distillation properties.

X1.8.4 For sea-level areas outside of the United States where vapor pressure requirements are not as restrictive as those specified by EPA, the following ambient temperatures are for guidance in selecting the appropriate alphanumeric designation:

Alphanumeric Volatility Designation	10th Percentile 6-h Minimum Daily Temperature, °C (°F)	90th Percentile Maximum Daily Temperature, °C (°F)
A-1	>16 (60)	≥43 (110)
B-2	>10 (50)	<43 (110)
C-3	>4 (40)	<36 (97)
D-4	>–7 (20)	<29 (85)
E-5	≤–7 (20)	<21 (69)

The 6-h minimum temperature is the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. The 6-h minimum temperature provides information on the cold-soak temperature experienced by a vehicle. The 10th percentile of this temperature statistic indicates a 10 % expectation that the 6-h minimum temperature will be below this value during a month. The 90th percentile maximum temperature is the highest temperature expected during 90 % of the days, and provides information relative to peak vehicle operating temperatures during warm and hot weather. For areas above sea level, the 10th percentile 6-h minimum temperature should be increased by 3.6°C/1000 m (2°F/1000 ft) of altitude, and the 90th percentile maximum should be increased by 4.4°C/1000 m (2.4°F/1000 ft) of altitude before comparing them to the sea level temperature. These corrections compensate for changes in fuel volatility caused by changes in barometric pressure due to altitude.

X1.9 Vapor Pressure

X1.9.1 The vapor pressure of fuel must be sufficiently high to ensure ease of engine starting, but it must not be so high as to contribute to vapor lock or excessive evaporative emissions and running losses.

X1.9.2 Test Methods D 4953, D 5190, D 5191, or D 5482 provide procedures for determining the vapor pressures of gasoline or gasoline-oxygenate blends.

X1.10 Vapor-Liquid Ratio

X1.10.1 Vapor-liquid ratio (V/L) is the ratio of the volume of vapor formed at atmospheric pressure to the volume of fuel tested in Test Method D 2533. The V/L increases with temperature for a given fuel. Because some oxygenates are miscible with the glycerin confining fluid, Test Method D 2533 has been modified so mercury can also be used as a confining fluid. Either procedure may be used for determining V/L of gasoline. The mercury confining fluid shall be used for gasoline-oxygenate blends. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. Test Method D 5188 is applicable to both gasoline and gasoline-oxygenate blends.

X1.10.2 The temperature of the fuel system and the V/L that can be tolerated without vapor lock vary from vehicle to vehicle and with operating conditions. The tendency of a fuel to cause vapor lock, as evidenced by loss of power during full-throttle accelerations, is indicated by the gasoline temperature at a V/L of approximately 20. A similar relationship for gasoline-oxygenate blend has also been determined. The temperature at which the maximum V/L is specified for each gasoline volatility class is based on the ambient temperatures and the altitude associated with the use of the class.

X1.11 Vapor-Liquid Ratio (Estimated)

X1.11.1 Three techniques for estimating temperature-V/L values using vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) results are given in Appendix X2; they apply to gasoline only.
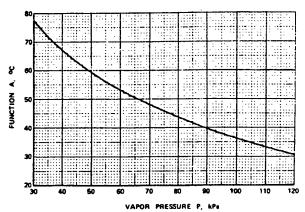
X1.12 Distillation

X1.12.1 Test Method D 86 for distillation provides another measure of the volatility of fuels. Table 1 designates the limits for endpoint temperature and the temperatures at which 10 %, 50 %, and 90 % by volume of the fuel is evaporated. These distillation characteristics, along with vapor pressure and *V/L* characteristics, affect the following vehicle performance characteristics: starting, driveability, vapor lock, dilution of the engine oil, fuel economy, and carburetor icing.

X1.12.2 The 10 % evaporated temperature of fuel should be low enough to ensure starting under normal temperatures.

X1.12.3 Fuels having the same 10 % and 90 % evaporated temperatures can vary considerably in driveability performance because of differences in the boiling temperatures of the intermediate components, or fractions. Driveability and idling quality are affected by the 50 % evaporated temperature. The 90 % evaporated and endpoint temperatures should be low enough to minimize dilution of the engine oil.

X1.12.4 The ASTM Driveability Task Force has determined from data collected by CRC and others that a relationship exists between fuel distillation temperatures and vehicle cold start and warm-up driveability performance. This relationship can be expressed by a Driveability Demerit model that can estimate vehicle driveability demerits during cold start and warm-up conditions. The predictive model is a function of ambient temperature and fuel volatility expressed as the distillation temperatures at which 10 %, 50 %, and 90 % by volume of the fuel is evaporated. The Driveability Index (DI = $1.5\,T_{10} + 3.0\,T_{50} + 1.0\,T_{90}$), as shown in Table 1, is a simplified and more easily applied form of the Driveability Demerit model. A more detailed explanation of the DI equation development can be found in SAE Paper 881668.[12]

X1.13 Corrosion

X1.13.1 Fuels must pass the copper strip corrosion test to minimize corrosion in fuel systems due to sulfur compounds in the fuel. Some fuels corrode fuel system metals other than copper, but there are no ASTM test methods to evaluate corrosion of these metals. Depending on the type and concentration of oxygenate, gasoline-oxygenate blends can corrode metals such as zinc, magnesium, aluminum, steel, and terne. However, at this time there is no test method with a known correlation to field performance. Consequently, additional corrosion tests are needed.

X1.14 Solvent-Washed Gum Content

X1.14.1 The test for solvent-washed gum content measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, non-volatile material such as additives, carrier oils used with additives, and heavier hydrocarbons such as diesel fuels, and so forth. Solvent-washed gum consists of fuel-insoluble gum and fuel-soluble gum. The fuel-insoluble

portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

X1.14.2 Solvent-washed gum can contribute to deposits on the surfaces of carburetors, fuel injectors, and intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum on malfunctions of modern engines is not well established and the current specification limit is historic rather than the result of recent correlative studies. It depends on where the deposits form; the presence of other deposit precursors, such as airborne debris, blowby and exhaust gas recirculation gases, and oxidized engine oil; and the amount of deposits.

X1.14.3 The difference between the unwashed and solvent-washed gum content values can be used to assess the presence and amount of nonvolatile material in the fuel. Additional analytical testing is required to determine if the material is additive, carrier oil, diesel fuel, and so forth.

X1.15 Sulfur

X1.15.1 The limit on sulfur content is included to protect against engine wear, deterioration of engine oil, and corrosion of exhaust system parts.

X1.16 Oxidation Stability

X1.16.1 The induction period as measured in the oxidation stability test is used as an indication of the resistance of fuel to gum formation in storage. Experience indicates that fuels with an induction period equal to or greater than that in Table 2 generally have acceptable short-term storage stability. However, correlation of the induction period with the formation of gum in storage can vary markedly under different storage conditions and with different fuels.

X1.17 Water Tolerance

X1.17.1 Water tolerance is the ability of a fuel to dissolve water without phase separation. It is not of concern for gasoline because of the very low solubility of water in hydrocarbons. Water tolerance is of some concern with gasoline-ether blends because of the limited solubility of ethers in water, but it is of great concern for gasoline-alcohol blends because of the very high solubility of alcohols in water. As such, Test Method D 6422 has been developed to determine the water tolerance (phase separation) characteristics of gasoline-alcohol blends. If the amount of water exceeds the water tolerance limit of the blend, the fuel will separate into a lower, alcohol-rich aqueous phase and an upper, alcohol-lean hydrocarbon phase. The resultant aqueous phase is not suitable as an automotive fuel and may be corrosive to many metals. Similarly, the hydrocarbon portion may also not be suitable as a fuel since removal of the alcohol component will change the volatility and antiknock characteristics.

X1.17.2 The most important factor, besides the quantity of water contacted, which governs the water tolerance of a fuel, is its temperature. As the temperature of the blend decreases, water tolerance decreases. Test Method D 6422 is intended to determine the ability of gasoline-alcohol blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be exposed in use. Some other

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[12] Barker, D. A., Gibbs, L. M., and Steinke, E. D., "The Development and Implementation of the ASTM Driveability Index," SAE Paper 881668, 1988. Available from Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096.

factors that affect water tolerance are alcohol concentration and aromatics content of the fuel.

X1.17.3 With some gasoline-oxygenate blends, formation of a haze may occur when filling a storage tank that contains water bottoms, while commingling of gasoline-oxygenate blends with gasoline, or when a sufficient decrease in temperature occurs. However, the haze may not be stable and the fuel will clear usually in a short period of time.

X1.17.4 A more critical water tolerance concern is the potential increase in storage tank water bottoms. This can occur when some gasoline-oxygenate blends and gasoline-alcohol blends in particular are added to a tank that contains sufficient water to extract some or all of the oxygenate component from the fuel.

X2. ESTIMATING TEMPERATURE-*V/L* VALUES FOR GASOLINE

X2.1 Scope

X2.1.1 Three techniques are presented here for estimating temperature-*V/L* data from vapor pressure and distillation test results[13] on gasolines only. They are provided for use as a guideline when *V/L* data measured by Test Method D 2533 are not available. One method is designed for computer processing, one is a simpler linear technique, while the other is a nomogram form of this linear equation.

X2.1.2 These techniques are not optional procedures for measuring *V/L*. They are supplementary tools for estimating temperature-*V/L* relationships with reasonable accuracy when used with due regard for their limitations.

X2.1.3 Test Method D 2533 is the referee *V/L* procedure and shall be used when calculated values are questionable.

X2.1.4 These techniques are not intended for, nor are they necessarily applicable to, fuels of extreme distillation or chemical characteristics, such as would be outside the range of normal commercial motor gasolines. Thus, they are not applicable in all instances to gasoline blending stocks or specially blended fuels.

X2.2 Computer Method

X2.2.1 *Summary*—The values of four intermediate functions, *A, B, C,* and *D*, are derived from the gasoline vapor pressure and distillation temperatures at 10, 20, and 50 % evaporated. Values for *A, B, C,* and *D* can be obtained either from equations or from a set of charts. Sections X2.2.2.1-X2.2.2.3 provide *A, B, C,* and *D* values using SI units; X2.2.2.6-X2.2.2.8 provide *A, B, C,* and *D* values using inch-pound units. Estimated temperatures at a *V/L* of 4, 10, 20, 30, and 45 are then calculated from *A, B, C,* and *D*. Estimated temperatures at an intermediate *V/L* can be obtained by interpolation.

X2.2.2 *Procedure*:

X2.2.2.1 Establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:

FIG. X2.1 Function *A* versus Vapor Pressure *P*

E = distillation temperature, °C at 10 % evaporated,

F = distillation temperature, °C at 20 % evaporated,

G = distillation temperature, °C at 50 % evaporated,

$$H = G - E, °C, \qquad (X2.1)$$

P = vapor pressure, kPa,

$$Q = F - E, °C, \text{ and} \qquad (X2.2)$$

$R = H/Q$, except that if H/Q is greater than 6.7, make $R = 6.7$.

$$(X2.3)$$

X2.2.2.2 If *A, B, C,* and *D* are to be calculated, use the following equations:

$$A = 102.859 - 1.36599P + 0.009617\,P^2 - 0.000028281P^3 + 207.0097/P \qquad (X2.4)$$

$$B = -5.36868 + 0.910540Q - 0.040187\,Q^2 + 0.00057774Q^3 + 0.254183/Q \qquad (X2.5)$$

$$S = -0.00525449 - 0.3671362/(P - 9.65) - 0.812419/(P - 9.65)^2 + 0.0009677R - 0.0000195828R^2 - 3.3502318R/P^2 + 1241.1531R/P^4 - 0.06630129R^2/P + 0.00627839R^3/P + 0.0969193R^2/P^2 \qquad (X2.6)$$

$$C = 0.34205P + 0.55556/S \qquad (X2.7)$$

$$D = 0.62478 - 0.68964R + 0.132708R^2 - 0.0070417R^3 + 5.8485/R \qquad (X2.8)$$

X2.2.2.3 If *A, B, C,* and *D* are to be obtained from charts, read them from Figs. X2.1-X2.4, respectively.

X2.2.2.4 Calculate the estimated temperature (°C or °F) at *V/L* ratios 4, 10, 20, 30, and 45 from the following equations:

$$T4 = A + B \qquad (X2.9)$$

---
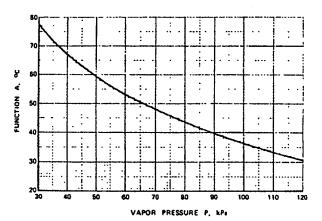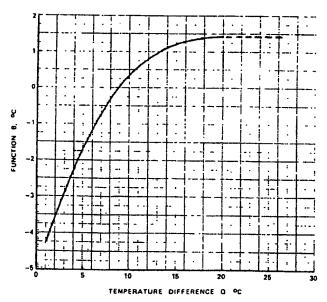
[13] A correlation of temperature-*V/L* ratio data with vapor pressure and distillation data was developed in 1943 and restudied in 1963 by panels of the Coordinating Research Council, Inc. See "Correlation of Gasoline Vapor Forming Characteristics with Inspection Test Data," *CRC Report No. 159*, Jan. 28, 1943 (or SAE Transaction, Vol 52, August 1944, pp. 364–367) and "Study of CRC Calculated Temperature-*V/L* Technique," *CRC Report No. 370*, February 1963. The CRC correlation was modified by a task group of Subcommittee A of Committee D02 to adapt it for computer processing, as well as the linear equation and the nomogram.
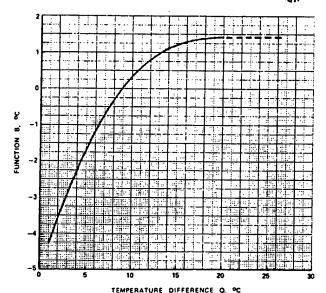
FIG. X2.2 Function B versus Distillation Temperature Difference Q
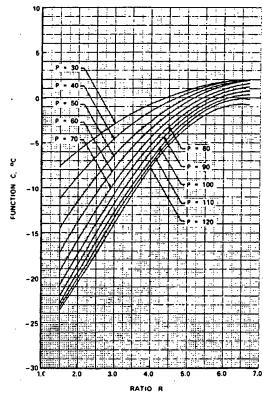

FIG. X2.3 Function C versus Ratio R and Vapor Pressure P

$$T45 = F + 0.125H + C \qquad (X2.10)$$

$$T10 = T4 + 0.146341\,(T45 - T4) + D \qquad (X2.11)$$

$$T20 = T4 + 0.390244\,(T45 - T4) + 1.46519D \qquad (X2.12)$$
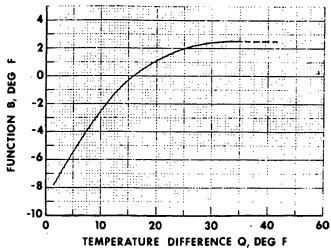
$$T30 = T4 + 0.634146\,(T45 - T4) + D \qquad (X2.13)$$
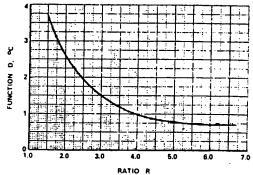
FIG. X2.4 Function D versus Ratio R

where:

$T4$, $T10$, $T20$, $T30$, and $T45$ are estimated temperatures at V/L ratios, 4, 10, 20, 30, and 45, respectively.

X2.2.2.5 If the temperature at an intermediate V/L ratio is to be estimated, either plot the values calculated in X2.2.2.4 and read the desired value from a smooth curve through the points, or use the Lagrange interpolation formula as follows:

$$
\begin{aligned}
TX = \; & T4\left(\frac{X-10}{4-10} \times \frac{X-30}{4-30} \times \frac{X-45}{4-45}\right) \\
& + T10\left(\frac{X-4}{10-4} \times \frac{X-30}{10-30} \times \frac{X-45}{10-45}\right) \\
& + T30\left(\frac{X-4}{30-4} \times \frac{X-10}{30-10} \times \frac{X-45}{30-45}\right) \\
& + T45\left(\frac{X-4}{45-4} \times \frac{X-10}{45-10} \times \frac{X-30}{45-30}\right)
\end{aligned}
\qquad (X2.14)
$$

where:

X = the desired V/L ratio between 4 and 45, and
TX = the estimated temperature at V/L ratio X.

X2.2.2.6 If inch-pound units are used, establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:

E = distillation temperature, °F at 10 % evaporated,

F = distillation temperature, °F at 20 % evaporated,

G = distillation temperature, °F at 50 % evaporated,

$$H = G - E, \,°F \qquad (X2.15)$$

P = vapor pressure, psi,

$$Q + F - E, \,°F, \text{ and} \qquad (X2.16)$$

$R = H/Q$, except that if H/Q is greater than 6.7, make R
= 6.7. $\qquad (X2.17)$

X2.2.2.7 If A, B, C, and D are to be calculated in inch-pound units, use the following equations:

$$A = 217.147 - 16.9527P + 0.822909P^2 - 0.0166849P^3 + 54.0436/P \qquad (X2.18)$$

$$B = -9.66363 + 0.910540Q - 0.0223260Q^2 + 0.000178314Q^3 + 0.823553/Q \qquad (X2.19)$$

$$S = -0.00525449 - 0.0532486/(P - 1.4) - 0.0170900/(P - 1.4)^2 + 0.0009677R -$$

FIG. X2.5 Function *A* versus Vapor Pressure *P*

FIG. X2.6 Function *B* versus Distillation Temperature Difference *Q*

$$0.0000195828R^2 - 0.0704753R/P^2 + 0.549224R/P^4$$
$$- 0.00961619R^2/P + 0.000910603R^3/P$$
$$+ 0.00203879R^2/P^2 \tag{X2.20}$$

$$C = 4.245P + 1.0/S \tag{X2.21}$$

$$D = 1.12460 - 1.24135R + 0.238875R^2$$
$$- 0.0126750R^3 + 10.5273/R \tag{X2.22}$$

X2.2.2.8 If *A*, *B*, *C*, and *D* are to be obtained from charts in inch-pound units, read them from Figs. X2.5-X2.8, respectively.

X2.2.2.9 Calculate the estimated temperatures, °F, at *V/L* ratios 4, 10, 20, 30, and 45 using the equations in X2.2.2.4 and X2.2.2.5.

X2.3 Linear Equation Method

X2.3.1 *Summary*—As given, these two equations provide only the temperatures (°C or °F) at which a *V/L* value of 20 exists. They make use of two points from the distillation curve, T_{10} and T_{50} (°C or °F), and the vapor pressure (kPa or psi) of the gasoline with constant weighting factors being applied to each. Experience has shown that data obtained with these simple linear equations generally are in close agreement with those obtained by the computerized version given above. The limitations pointed out in X2.1.1-X2.1.4 must be kept in mind when use is made of this procedure.

X2.3.2 *Procedure*—Obtain 10 % evaporated and 50 % evaporated points from the distillation curve (Test Method D 86) along with the vapor pressure value (Test Methods D 4953, D 5190, D 5191, or D 5482); apply these directly in the equation.

$$T_{V/L=20} = 52.47 - 0.33 \text{ (VP)} + 0.20 T_{10} + 0.17 T_{50} \tag{X2.23}$$

where:
$T_{V/L = 20}$ = temperature, °C, at *V/L* of 20:1,
VP = vapor pressure, kPa,
T_{10} = distillation temperature, °C, at 10 % evaporated, and
T_{50} = distillation temperature, °C, at 50 % evaporated.

FIG. X2.7 Function *C* versus Ratio *R* and Vapor Pressure *P*
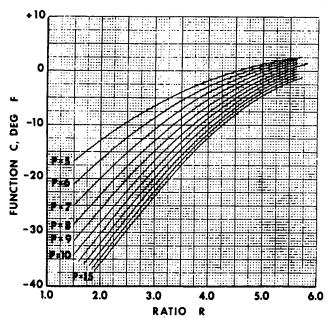
or in the inch-pound customary unit equation:

$$T_{V/L=20} = 114.6 - 4.1 \text{ (VP)} + 0.20 T_{10} + 0.17 T_{50} \tag{X2.24}$$

where:
$T_{V/L = 20}$ = temperature, °F, at *V/L* of 20:1,
VP = vapor pressure, psi,
T_{10} = distillation temperature, °F, at 10 % evaporated, and
T_{50} = distillation temperature, °F, at 50 % evaporated.

X2.4 Nomogram Method
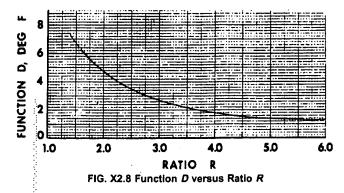
X2.4.1 *Summary*—Two nomograms have been developed and are included in this specification (Figs. X2.9 and X2.10) to provide the same function as the linear equations procedure

FIG. X2.8 Function *D* versus Ratio *R*

outlined above. Fig. X2.9 is in SI units and Fig. X2.10 is in inch-pound units. The nomograms are based on the two equations and the same limitations apply to their use in estimating *V/L* (20) temperatures.

X2.4.2 *Procedure*—Obtain 10 % evaporated and 50 % evaporated points from the distillation curve (Test Method D 86) along with the vapor pressure value (Test Methods D 4953, D 5190, D 5191, or D 5482). Select the SI unit (Fig. X2.9) or inch-pound unit (Fig. X2.10) nomogram based on the units of T_{10}, T_{50}, and VP. Using a straightedge, locate the intercept on the line between the "T_{10} and T_{50}" scales after selecting the applicable T_{10} and T_{50} values. From this intercept and the proper point on the "VP" scale, a second intercept can be obtained on the "$T_{V/L = 20}$" scale to provide the desired value directly.

X2.5 Precision

X2.5.1 The precision of agreement between temperature-*V/L* data estimated by any one of these three techniques and data obtained by Test Method D 2533 has not been established.

NOMOGRAM SOLVES EQUATION

$T_{V/L=20} = 52.47 - 0.33\ VP + 0.20\ T_{10} + 0.17\ T_{50}$

where:

$T_{V/L=20}$ = TEMPERATURE (°C) FOR VAPOR/LIQUID RATIO OF 20:1
T_{10} = 10 % EVAPORATION POINT (°C)
T_{50} = 50 % EVAPORATION POINT (°C)
VP = VAPOR PRESSURE (kPa)

EXAMPLE

GIVEN

VP — 82 kPa
T_{10} — 45°C
T_{50} — 110°C

SOLUTION

$T_{VL \cdot 20}$ · 53.1

FIG. X2.9 Relationship Between Gasoline Volatility and Temperature for *V/L* Ratio at Sea Level—SI Units

NOMOGRAM SOLVES EQUATION T_{10}
$T_{V/L-20}$ = 114.6 – 4.1 VP + 0.20 T_{10} + 0.17 T_{50}
where:
$T_{V/L-20}$ = TEMPERATURE (°F) FOR VAPOR/LIQUID RATIO OF 20:1
T_{10} = 10 % EVAPORATION POINT (°F)
T_{50} = 50 % EVAPORATION POINT (°F)
VP = VAPOR PRESSURE (psi)

FIG. X2.10 Relationship Between Gasoline Volatility and Temperature for V/L Ratio of 20 at Sea Level—Inch-Pound Units

X3. SUMMARY OF EPA REGULATIONS APPLICABLE TO SPARK-IGNITION ENGINE FUEL

X3.1 EPA Applicable Vapor Pressure Standards

X3.1.1 Under authority of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) issued, effective May 1992, vapor pressure control standards for leaded and unleaded gasoline and leaded and unleaded gasoline-oxygenate blends. Some states, notably California, have more restrictive vapor pressure limits.

X3.1.2 Details of the EPA regulations and test methods are available in Part 80 of Title 40 of the Code of Federal Regulations (40 CFR Part 80). For specific state vapor pressure regulations, the state of interest should be contacted.

X3.1.3 The EPA maximum vapor pressure limits of 7.8 psi and 9.0 psi are shown in Table 1 as Classes AA and A, respectively. The EPA requirements for each distribution area are shown in Table 4 for the period May 1 through September 15. For the month of May, the EPA limits only apply to finished gasoline and gasoline-oxygenate blend tankage at refineries, importers, pipelines, and terminals. For the period June 1 through September 15, the EPA limits apply to all locations of the distribution system. Footnotes D through F of Table 4 indicate the ozone nonattainment areas which are limited to 7.8 psi maximum and the appropriate vapor lock protection class.

California has controls that vary for the different air basins from as early as March 1 at refineries through as late as October 31. There are no EPA vapor pressure limits for the states of Alaska or Hawaii.

X3.1.4 EPA regulations allow 1.0 psi higher values for gasoline-ethanol blends than the EPA limits shown in Table 1 and Table 4 for the period May 1 through September 15. To qualify, the gasoline-ethanol blends must contain 9 to 10 volume % ethanol. Higher vapor pressure limits for gasoline-ethanol blends under state regulations vary for other time periods, and specific states of interest should be contacted to determine if higher limits apply.

X3.2 EPA Lead and Phosphorus Regulations

X3.2.1 *Unleaded Fuel*—The intentional addition of lead or phosphorus compounds to unleaded fuel is not permitted by the EPA. EPA regulations limit their maximum concentrations to 0.05 g lead/U.S. gal (0.013 g/L) and 0.005 g of phosphorus/ U.S. gal (0.0013 g/L) (see Test Method D 3231), respectively.

X3.2.2 *Leaded Fuel*—EPA regulations after December 31, 1995 prohibit the sale, supply, dispensing, transporting, or introducing into commerce a fuel for use in any motor vehicle

which is produced with the use of lead additives or which contains more than 0.05 g lead/U.S. gal (0.013 g/L).

X3.2.2.1 The regulations define motor vehicle to include any self-propelled vehicle designed for transporting persons or property on a street or highway.

X3.2.2.2 The regulations do not prohibit the use of lead additives in fuel used in aircraft, racing cars, and nonroad engines, such as farm equipment engines and marine engines.

X3.3 EPA Oxygenate Regulations Applicable to Unleaded Gasoline-Oxygenate Blends

X3.3.1 *Substantially Similar Rule*:

X3.3.1.1 Section 211(f) (1) of the Clean Air Act prohibits introducing into commerce or increasing the concentration in use of, any fuel or fuel additive, which is not substantially similar to any fuel or fuel additive utilized for emissions certification of any model year 1975, or subsequent model year vehicle or engine, unless a waiver is obtained from the EPA.

X3.3.1.2 Gasoline-oxygenate blends are considered "substantially similar" if the following criteria are met.

(1) The fuel must contain carbon, hydrogen, and oxygen, nitrogen, or sulfur, or combination thereof, exclusively, in the form of some combination of the following:

(a) Hydrocarbons;
(b) Aliphatic ethers;
(c) Aliphatic alcohols other than methanol;
(d) (i) Up to 0.3 volume % methanol;
(ii) Up to 2.75 volume % methanol with an equal volume of butanol, or higher molecular weight alcohol;

(2) The fuel must contain no more than 2.0 mass % oxygen except fuels containing aliphatic ethers and/or alcohols (excluding methanol) must contain no more than 2.7 mass % oxygen.

(3) The fuel must possess, at the time of manufacture, all of the physical and chemical characteristics of an unleaded gasoline as specified by Specification D 4814 – 88 for at least one of the Seasonal and Geographical Volatility Classes specified in the standard.

NOTE X3.1—Opinion varies as to whether the EPA "substantially similar" rule requires unleaded gasolines that do not contain oxygenates to meet ASTM specifications.

X3.3.2 *Waivers*:

X3.3.2.1 EPA has issued waivers for blends of gasoline and ethanol (gasohol), gasoline and ethanol with cosolvents, and gasoline and methanol with cosolvents that are less limiting than the "substantially similar" rule. For the latest listing of waivers, EPA should be contacted.

X3.3.2.2 Gasoline-ethanol blends are not required by EPA to meet Specification D 4814 volatility limits (see X3.1.4 for vapor pressure limits). EPA has specified in all other waivers that the volatility of the finished gasoline-oxygenate blend must comply with Specification D 439 or D 4814 climatic and geographical limits.

X3.4 EPA Reformulated Gasoline (RFG)

X3.4.1 Reformulated gasoline (RFG) is a spark-ignition engine fuel formulated to reduce motor vehicle emissions of toxic and tropospheric ozone-forming compounds. The Clean Air Act Amendments of 1990 require that RFG be sold in nine metropolitan areas with the worst summertime ozone levels. Other areas that do not meet ambient ozone standards may petition EPA to require RFG. The various RFG regulations have been established by the EPA. EPA has also placed limits on conventional gasoline sold in the rest of the U.S. to prevent RFG producers from using conventional gasoline as an outlet for undesirable fuel components (anti-dumping requirements). The EPA requirements became effective at the retail level on January 1, 1995.

X3.4.2 The characteristics of reformulated spark-ignition engine fuel, beyond those described by this specification, are described in the research report on reformulated spark-ignition engine fuel.[2] The research report also includes information on California Air Resources Board Phase 2 gasoline requirements, which are more restrictive than the EPA RFG requirements and take effect at the retail level on June 1, 1996.

X3.5 EPA Certification Standards for Deposit Control Gasoline Additives

X3.5.1 Beginning August 1, 1997, except for some fuel specific certifications, fuel sold or transferred to the ultimate consumer must contain detergent additive(s) meeting the EPA certification requirements. The regulation applies to fuels whether intended for on-highway or nonroad use, including conventional, reformulated, oxygenated, and leaded gasolines, as well as fuels used in marine service, and the gasoline component of M85 and E85 fuel alcohols. Racing fuel for non-highway use in racing vehicles and aviation fuel used in aircraft are exempted. Fuels used for research, development, and testing and federal emissions certification fuels can be exempted.

X3.5.2 As of July 1, 1997, only certified detergents may be used by detergent blenders, and distributors may only sell or transfer fuel that is properly additized with certified detergents. Detergent additives may be certified for nationwide use, for geographical use based on Petroleum Administration Districts for Defense (PADDs), or for a fuel-specific option for segregated gasoline pools. Certification sub-options allow a detergent to be certified for use in premium-grade, nonoxygenated, or oxygenate-specific fuel. A California Air Resources Board additive certification will be accepted for fuel additized or used only in California. Specific minimum fuel properties (aromatics, sulfur content, olefins content, and 90 % evaporated point) for each option are required for certification and the certification fuels must also meet the requirements of Specification D 4814-95c. For some options, the addition of 10 volume % ethanol is required for certification fuel. Other oxygenates may also be required. Testing is required to demonstrate that the certification fuels without additives form a minimum level of intake valve deposits if specially formulated from refinery blend stocks. Such deposit demonstration testing is not required for test fuels sampled directly from finished fuels, fuel-specific test fuels, CARB-based certifications, and leaded gasoline certifications.

X3.5.3 For additive certification, the test fuel containing the detergent additive(s) must form less than 100 mg/valve average intake valve deposit weight after 10 000 miles of testing in accordance with Test Method D 5500-94. In addition, after

10 000 miles of testing, there may be no more than 5 % flow restriction in any one fuel injector in accordance with Test Method D 5598-94.

X3.6 EPA Gasoline Sulfur Requirements (Tier 2)[14]

X3.6.1 Beginning in 2004, the basic EPA sulfur regulations require refiners to meet a corporate pool annual average sulfur maximum level of 120 parts per million (ppm), with a per gallon cap of 300 ppm. A provision in the rules allows a refinery to exceed the 300 ppm cap up to a maximum of 350 ppm for 2004. EPA has taken into account a 28 ppm test reproducibility which translates into a downstream enforcement standard of 378 ppm maximum (350+28). Anyone taking advantage of producing gasoline in excess of 300 ppm has to make up for the excess in their 2005 cap. For 2005, the corporate pool annual average decreases to 90 ppm maximum, the per gallon cap is at 300 ppm, and a refinery annual average maximum limit of 30 ppm is added. The downstream enforcement standard lowers to 326 ppm (300 ppm refinery cap plus 26 ppm test reproducibility). For 2006 and later, the refinery annual average remains at 30 ppm maximum, the per gallon cap is reduced to 80 ppm, and there no longer is a corporate pool annual average limit. The downstream enforcement standard is reduced to 95 ppm maximum (80 ppm refinery cap plus 15 ppm test reproducibility).

X3.6.2 Also beginning in 2004, there is a separate set of standards for a Geographical Phase-In Area Program (GPA)

which consists of the states of Alaska, Colorado, Idaho, Montana, New Mexico, North Dakota, Utah, and Wyoming, and selected regions of Arizona, Nebraska, Nevada, Oregon, South Dakota and Washington. The 2004 limits are the same as for the basic program, except there also is a 150 ppm maximum refinery annual average. For 2005, the refinery annual average remains at 150 ppm maximum while the corporate pool annual average and per gallon cap are the same as the basic program. If more than 50% of a refiner's gasoline is GPA in 2004 or 2005, the corporate pool average does not apply in 2004-2005. For 2006, the corporate pool annual average is eliminated while the other limits remain the same as for 2005. For 2007, the limits become the same as for the basic program with the refinery annual average at 30 ppm maximum and the per gallon cap at 80 ppm. The downstream enforcement level is at 95 ppm maximum (80 ppm refinery cap plus 15 ppm reproducibility tolerance). However, there is a process to obtain a two-year extension (through 2007 and 2008) of the 2006 limits where the GPA refinery agrees to also produce 15 ppm maximum sulfur diesel fuel beginning in 2006.

X3.6.3 For refiners that qualify for small refiner status, another set of sulfur limits applies for the period 2004 through 2007. The annual average sulfur level standard for each refinery is determined based on the refinery's 1997-1998 sulfur level baseline and the maximum ranges from 30 ppm to 300 ppm. The sulfur cap is similarly based and can range from 300 ppm to 450 ppm. Small refiners may also obtain a three-year extension (through 2008, 2009, and 2010) of the 2007 limits where the small refiner agrees to produce 15 ppm maximum sulfur diesel fuel beginning in 2006.

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[14] Details of the sulfur regulations, including definitions, specific limits, effective dates, exceptions, and enforcement, are available in Parts 80.190 through 80.415 of Title 40 of the Code of Federal Regulations (40 CFR Parts 80.190-80.415).

X4. METHOD FOR CALCULATING MASS PERCENT OXYGEN OF GASOLINE-OXYGENATE BLENDS

X4.1 Scope

X4.1.1 Test Method D 4815 provides a procedure for calculating the mass oxygen content of fuels using oxygenate concentration in mass percent. When oxygenate concentration in mass percent is not available, the oxygen concentration of these fuels can be determined indirectly by: (1) measuring the volume concentration of the oxygenates in the blend, which may be reported from Test Method D 4815 or equivalent method, (2) measuring the density or relative density of the blend, (3) converting the oxygenate concentrations from volume to mass concentrations, and (4) converting the mass oxygenate concentrations to mass oxygen concentrations using the oxygen mass fractions of the oxygenates present.

X4.2 Procedure

X4.2.1 The following steps are used to determine the total mass oxygen concentration of gasoline-oxygenate blends when indirect calculation is necessary.

X4.2.1.1 Determine the volume concentrations of oxygenates in a gasoline-oxygenate blend (Test Method D 4815 or equivalent test method).

X4.2.1.2 Determine the density or relative density of the gasoline-oxygenate blend (Test Methods D 287, D 1298, or D 4052).

X4.2.1.3 The oxygen mass percent of the gasoline-oxygenate blend is calculated using the following general equation. The densities or relative densities and oxygen mass fractions of a number of pure oxygenates are provided in Table X4.1 for use in Eq X4.1. The choice of density or relative density must be the same as determined in X4.2.1.2 for the gasoline-oxygenate blend.

$$\text{Oxygen, Mass \%} = \frac{V_1 \times d_1 \times O_1 + V_2 \times d_2 \times O_2 \dots + V_n \times d_n \times O_n}{V_b \times d_b} \times 100$$

(X4.1)

TABLE X4.1 Densities, Relative Densities, and Oxygen Mass Fractions of Pure Oxygenates

Oxygenate	Density, g/mL 20°C (68°F)	Relative Density 15.56/15.56°C (60/60°F)	Oxygen Mass Fraction
Methyl Alcohol	0.7913	0.7963	0.4993
Ethyl Alcohol	0.7894	0.7939	0.3473
n-Propyl Alcohol	0.8038	0.8080	0.2662
Isopropyl Alcohol	0.7855	0.7899	0.2662
n-Butyl Alcohol	0.8097	0.8137	0.2158
Isobutyl Alcohol	0.8016	0.8058	0.2158
sec-Butyl Alcohol	0.8069	0.8114	0.2158
tertiary-Butyl Alcohol	0.7866[A]	0.7922[A]	0.2158
Methyl tertiary-Butyl Ether	0.7406	0.7460	0.1815
Ethyl tertiary-Butyl Ether	0.7399	0.7452	0.1566
tertiary-Amyl Methyl Ether	0.7707	0.7758	0.1566
tertiary-Hexyl Methyl Ether	0.7815	0.7860	0.1377
Diisopropyl Ether	0.7235	0.7282	0.1566

[A] Extrapolated, below freezing temperature.

where:
V_n = volume % of oxygenates 1 through n,
d_n = density or relative density of oxygenates 1 through n,
O_n = mass fraction oxygen in oxygenates 1 through n,
V_b = volume % of gasoline-oxygenate blend = 100, and
d_b = density or relative density of gasoline-oxygenate blend.

X4.3 Example Calculation

X4.3.1 Assume that a gasoline-oxygenate blend is reported to contain 9.5 volume % ethanol and 2.0 volume % methyl tertiary-butyl ether and that the relative density of the blend is measured to be 0.7450, 15.56/15.56°C (60/60°F).

X4.3.2 Using the relative density and oxygen mass fraction data for ethanol and methyl tertiary-butyl ether from Table X4.1, the following mass % oxygen is calculated for this gasoline-oxygenate blend.

$$\text{Oxygen, Mass \%} = \qquad\qquad (X4.2)$$

$$\frac{9.5 \times 0.7939 \times 0.3473 + 2.0 \times 0.7460 \times 0.1815}{100 \times 0.7450} \times 100 = 3.88$$

X4.4 Precision

X4.4.1 The precision of this calculation method is a function of the individual precisions of density or relative density (Test Methods D 287, D 1298, or D 4052) and oxygenate analysis (Test Method D 4815 or equivalent). Because the repeatability and reproducibility vary with the analyses used, no estimate is provided.

X5. MICROBIAL CONTAMINATION

X5.1 Uncontrolled microbial contamination in fuel systems may cause or contribute to a variety of problems including increased corrosivity, and decreased stability, filterability, and caloric value. Microbial processes in fuel systems may also cause or contribute to system damage.

X5.2 Because the microbes contributing to the aforementioned problems may not be present in the fuel itself, no microbial quality criterion for fuels is recommended. However, it is important that personnel responsible for fuel quality understand how uncontrolled microbial contamination may affect fuel quality.

X5.3 Guide D 6469 provides personnel with limited microbiological background an understanding of the symptoms, occurrences, and consequences of chronic microbial contamination. Guide D 6469 also suggests means for detecting and controlling microbial contamination in fuels and fuel systems.

X6. FUEL FILTRATION

X6.1 During the distribution of spark-ignition fuels, it is possible for them to become contaminated with potential filter blocking materials. While proper handling will minimize the contamination levels, it is recommended that all fuel dispensers be equipped with filters of 10 µm or less nominal pore size at point of delivery to the customer.

D 4814 – 04a

SUMMARY OF CHANGES

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D 4814–04) that may impact the use of this standard. (Approved July 1, 2004.)

(1) Added new footnote to Table 2.
(2) Added new X3.6.
(3) Changed Table 6 for Colorado.

(4) Changed sulfur limit for unleaded gasoline to comply with Federal Tier 2 sulfur regulations.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D 4814–03a) that may impact the use of this standard. (Approved June 1, 2004.)

(1) Added Test Method D 5599 to 5.1 and the Referenced Documents.

The Stamp of the Patent and Trademark Office, placed hereon, acknowledges receipt of:

Applicant:	Lieder, et al.	**Serial No.**	09/556,852
Attorney:	John Wilson Jones	**Attorney File No.**	013129-00025
Date:	December 13, 2004		

Title: "Gasoline-Oxygenate Blend and Method of Producing the Same"

Transmittal Form; Petition for One-Month Extension; Amendment and Response to Office Action Dated 10 September 2004; Declaration of Charles A. Lieder, Ph.D.;Return Receipt Postcard.

TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

Application Number	09/556,852
Filing Date	April 21, 2000
First Named Inventor	Charles A. LIEDER
Art Unit	1714
Examiner Name	C. TOOMER
Attorney Docket Number	013129-00025

Total Number of Pages in This Submission | 23+

ENCLOSURES   *(Check all that apply)*

- ☐ Fee Transmittal Form
  - ☐ Fee Attached
- ☐ Amendment/Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☐ Extension of Time Request
- ☐ Express Abandonment Request
- ☐ Information Disclosure Statement
- ☐ Certified Copy of Priority Document(s)
- ☐ Reply to Missing Parts/ Incomplete Application
  - ☐ Reply to Missing Parts under 37 CFR 1.52 or 1.53

- ☐ Drawing(s)
- ☐ Licensing-related Papers
- ☐ Petition
- ☐ Petition to Convert to a Provisional Application
- ☐ Power of Attorney, Revocation Change of Correspondence Address
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  - ☐ Landscape Table on CD

Remarks

- ☐ After Allowance Communication to TC
- ☐ Appeal Communication to Board of Appeals and Interferences
- ☑ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
- ☐ Proprietary Information
- ☐ Status Letter
- ☑ Other Enclosure(s) (please identify below):
  --Itemized Return Postcard

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	Locke Liddell & Sapp, LLP
Signature	
Printed name	Steven S. Boyd
Date	2/28/2006	Reg. No.	42,353

CERTIFICATE OF TRANSMISSION/MAILING

I hereby certify that this correspondence is being facsimile transmitted to the USPTO or deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date shown below:

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Typed or printed name	Steven Boyd	Date	2/28/2006

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